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Quality Assurance Plan: Love Canal Study
Appendix B. Analytical Procedures

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Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

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LOVE CANAL STUDY
LC 1-619-026

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APPENDIX B
ANALYTICAL PROCEDURES

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

The four volumes in this set comprise the working guideline documents for the Love Canal Study. The documents were developed to direct both the prime contractor and subcontractors while performing for the Environmental Protection Agency. Detailed procedures for each analysis type are described. Procedures for all field sampling are also described. Quality assurance plans submitted by each subcontractor and approved by the prime contractor are provided. A description of the document control procedure, chain-of-custody procedure, various quality control procedures, and other study operational procedures are provided.

Together the four documents provide a "work plan" for the Love Canal effort. Since the volumes were developed prior to the actual field sampling, no environmental results are included.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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QUALITY ASSURANCE PLAN
LOVE CANAL STUDY
APPENDIX B

REVISION 0 - ERRATA SHEET

Section 1.3.1, Page 2, A, line 6:
Change "4°C" to "ambient temperature."

Section 1.3.2, Page 1, A, bullet 3:
Add "α,α'dichloroxylene will be used."

Section 2.1, Page 1, first paragraph:
Add to pollutant class listings 2.7 and 2.8, "groundwater only."

Add new pollutant classes,
"2.11 pH - groundwater only
2.12 Conductivity - groundwater only."

Section 3.1, Page 1, first paragraph:
Add new pollutant class, "3.7 Radioactivity."

Section 3.3.2, Page 1, C, line 1:
Change "sample" to "concentrated sample extract."

Section 3.5.1, Page 2, 3 (first paragraph):
Delete entire paragraph.

Section 3.5.1, Page 3, indented paragraph a, line 6:
Change "of" to "to."

Section 4.2, Pages 1, 2, 3, section numbering:
Change "4.2" to "4.2.1."

Section 4.2.1, Page 1, line 1:
Change "ORGANIC COMPOUNDS" to "SEMIVOLATILES AND PESTICIDES IN ANIMAL TISSUE."

Section 5.1, Page 2, BIOTA, Volatiles:
Change Section "4.2" to "4.3."
Add Data reporting forms, "J15, J16."

Section 5.1, Page 2, BIOTA:
Add this listing,
"Metals"   4.4, 4.5   J07, J14"

Section 7.0, Page 1, listing 7.6, DIOXINS:
Change "1 of 1" to "1 of 25."

APPENDIX B

ANALYTICAL PROCEDURES

TABLE OF CONTENTS

Section			Page	Revision
1.0	AIR ANALYSIS			
	1.1	OVERVIEW	1 of 1	0
	1.2	VOLATILE ORGANIC COMPOUNDS ON TENAX		
		1.2.1 Analytical Procedures	1 of 4	0
		1.2.2 Quality Control Procedures	1 of 4	0
	1.3	PESTICIDES AND RELATED COMPOUNDS ON POLYURETHANE FOAM PLUGS		
		1.3.1 Analytical Procedures	1 of 13	0
		1.3.2 Quality Control Procedures	1 of 3	0
	1.4	METALS		
		1.4.1 Analytical Procedures	1 of 60	0
		1.4.2 Quality Control Procedures	1 of 3	0
	1.5	DIOXINS		
		1.5.1 Analytical Procedures	1 of 3	0
		1.5.2 Quality Control Procedures	1 of 3	0
2.0	WATER ANALYSIS			
	2.1	OVERVIEW	1 of 6	0
	2.2	VOLATILE ORGANICS		
		2.2.1 Analytical Procedures	1 of 1	0
		2.2.2 Quality Control Procedures	1 of 4	0
	2.3	SEMIVOLATILE ORGANICS		
		2.3.1 Analytical Procedures	1 of 8	0
		2.3.2 Quality Control Procedures	1 of 4	0
	2.4	PESTICIDES		
		2.4.1 Analytical Procedures	1 of 1	0
		2.4.2 Quality Control Procedures	1 of 2	0
	2.5	METALS		
		2.5.1 Analytical Procedures	1 of 37	0
		2.5.2 Quality Control Procedures	1 of 4	0
	2.6	ANIONS		
		2.6.1 Analytical Procedures	1 of 20	0
		2.6.2 Quality Control Procedures	1 of 3	0
	2.7	TOTAL ORGANIC CARBON		
		2.7.1 Analytical Procedures	1 of 4	0
		2.7.2 Quality Control Procedures	1 of 2	0
	2.8	TOTAL ORGANIC HALOGENS		
		2.8.1 Analytical Procedures	1 of 3	1
		2.8.2 Quality Control Procedures	1 of 2	0
	2.9	DIOXINS		
		2.9.1 Analytical Procedures	1 of 3	0
		2.9.2 Quality Control Procedures	1 of 3	0

TABLE OF CONTENTS (continued)

Section			Page	Revision
	2.10	RADIOACTIVITY		
		2.10.1 Analytical Procedures	1 of 1	0
		2.10.2 Quality Control Procedures	1 of 2	0
	2.11	pH		
		2.11.1 Analytical Procedures	1 of 4	0
		2.11.2 Quality Control Procedures	1 of 2	0
	2.12	CONDUCTIVITY		
		2.12.1 Analytical Procedures	1 of 6	0
		2.12.2 Quality Control Procedures	1 of 2	0
3.0	SOIL AND SEDIMENT ANALYSIS			
	3.1	OVERVIEW	1 of 1	0
	3.2	VOLATILES		
		3.2.1 Analytical Procedures	1 of 4	0
		3.2.2 Quality Control Procedures	1 of 3	0
	3.3	SEMIVOLATILES		
		3.3.1 Analytical Procedures	1 of 37	0
		3.3.2 Quality Control Procedures	1 of 4	0
	3.4	PESTICIDES		
		3.4.1 Analytical Procedures	1 of 17	0
		3.4.2 Quality Control Procedures	1 of 2	0
	3.5	METALS		
		3.5.1 Analytical Procedures	1 of 7	0
		3.5.2 Quality Control Procedures	1 of 3	0
	3.6	DIOXINS		
		3.6.1 Analytical Procedures	1 of 5	0
		3.6.2 Quality Control Procedures	1 of 3	0
	3.7	RADIOACTIVITY		
		3.7.1 Analytical Procedures	1 of 1	0
		3.7.2 Quality Control Procedures	1 of 2	0
4.0	BIOTA ANALYSIS			
	4.1	OVERVIEW	1 of 1	1
	4.2	SEMIVOLATILES AND PESTICIDES IN ANIMAL TISSUE		
		4.2.1 Analytical Procedures	1 of 3	0
		4.2.2 Quality Control Procedures	1 of 3	0
	4.3	VOLATILE ORGANICS IN FOODSTUFFS		
		4.3.1 Analytical Procedures	1 of 3	0
		4.3.2 Quality Control Procedures	1 of 3	0
	4.4	METALS IN HAIR		
		4.4.1 Analytical Procedures	1 of 2	0
		4.4.2 Quality Control Procedures	1 of 3	0
	4.5	METALS IN VEGETATION		
		4.5.1 Analytical Procedures	1 of 27	0
		4.5.2 Quality Control Procedures	1 of 3	0
	4.6	INTERFERON IN MOUSE CELLS		
		4.6.1 Analytical Procedures	1 of 13	0
		4.6.2 Quality Control Procedures	1 of 2	0

TABLE OF CONTENTS (continued)

Section		Page	Revision
5.0	DATA REPORTING FORMS		
	5.1 OVERVIEW	1 of 35	0
6.0	CHAIN-OF-CUSTODY PROCEDURES		
	6.1 DOCUMENT CONTROL PROCEDURES	1 of 4	0
	6.1.1 QA Project Plan	1 of 4	0
	6.1.2 Project Numbering Systems	1 of 4	0
	6.2 CHAIN-OF-CUSTODY PROCEDURES	1 of 7	0
	6.2.1 Sample Identification	1 of 7	0
	6.2.2 Sample Transfer Procedures/ Chain-of-Custody Records	2 of 7	0
	6.2.3 Custody Seals	6 of 7	0
	6.2.4 Custody of Shipped Samples	6 of 7	0
	6.2.5 Laboratory Custody Procedures	6 of 7	0
7.0	REFERENCE MATERIAL		
	7.1 METHOD 603 - ACROLEIN, ACRYLONITRITE	1 of 7	0
	7.2 METHOD 605 - BENZIDINES	1 of 4	0
	7.3 METHOD 608 - ORGANOCHLORINE PESTICIDES AND PCBs	1 of 10	0
	7.4 METHOD 624 - PURGEABLES	1 of 9	0
	7.5 METHOD 625 - BASE/NEUTRALS, ACIDS AND PESTICIDES	1 of 14	0
	7.6 DIOXINS	1 of 25	0
	7.7 QUALITATIVE ANALYSIS BY GC/MS	1 of 1	0
	7.8 METALS BY ATOMIC ABSORPTION SPECTROMETRY	1 of 83	0

Distribution of Appendix B

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1.0 AIR ANALYSIS

1.1 OVERVIEW

Air samples collected in the Love Canal area will be analyzed for a number of elements and organic compounds in order to determine the ambient levels of these substances. Collection methods have been specified for each of the three general classes of pollutants to be monitored, resulting in three distinct sample types.

1. Tenax Cartridges--used to collect volatile organic compounds by adsorption
2. Polyurethane Foam Plugs--used to collect pesticides and related organic compounds
3. Hi-volume (Hi-vol) Filters--to be analyzed for metals.

All quality control procedures specified by the analytical methods are to be followed; the following quality control procedures are a part of all analyses.

1. Method blanks
2. Replicate analyses
3. Laboratory control standards

Specific quality control requirements are detailed in each section.

Sample preservation procedures for Tenax cartridges and foam plugs consist of maintaining the samples at 4°C until analysis.

1.2 VOLATILE ORGANIC COMPOUNDS ON TENAX

1.2.1 Analytical Procedures

Ambient concentrations of selected volatile organic compounds are monitored by collection of integrated samples on Tenax® sorbent cartridges, using an appropriate air sampling system and subsequent analysis. The volatile organic constituents are determined by thermal desorption of the Tenax cartridges such that the desorbed organics are first cryogenically trapped and then flashed onto a capillary column for GC/MS analysis. The compounds listed below are to be analyzed either qualitatively or quantitatively, as designated:

Quantitative Analysis

- Benzene
- Carbon tetrachloride
- Chlorobenzene
- o-Chlorotoluene
- p-Chlorotoluene
- 1,2-Dibromoethane
- o-Dichlorobenzene
- p-Dichlorobenzene
- 1,1,2,2-Tetrachloroethylene
- Toluene

Qualitative Analysis

- Chloroform
- 1,2-Dichloroethane
- 2,4-Dichlorotoluene
- o-Chlorobenzaldehyde
- p-Chlorobenzaldehyde
- Benzyl Chloride (α-chlorotoluene)
- 1,1-Dichloroethane
- 1,1-Dichloroethylene (vinylidene chloride)
- 1,2-Dichloroethylene
- Dichloromethane
- Phenol
- o-Xylene
- m-Xylene
- p-Xylene

A. Sample Handling and Preservation

Tenax cartridges are received at the analytical laboratory as part of the chain-of-custody sequence described in Section 6.0 of this Appendix. Internal chain-of-custody must be maintained. These samples are to be kept at 4°C until the time of analysis. The cartridges are not to be removed from the sealed culture tube until the time of thermal desorption. All handling of the cartridges must be done wearing cloth gloves or using appropriate tongs to prevent contamination. All thermally desorbed cartridges are to be stored in their original culture tube container until notified of their disposition.

B. Apparatus

1. Desorption Equipment

- Thermal desorption and trapping apparatus (Nutech Model 320 Thermal Desorption System, or equivalent)
- Mass flow meter (Tylon Model FC 260, or equivalent), calibrated for He in the 0-10 cc/minute range
- Liquid nitrogen
- Ultrahigh purity helium
- Vacuum dewer
- Bubble meter

2. Gas Chromatograph

- Analytical gas chromatographic system with capillary inlet and oven temperature programming capability and amenable to interface with the above thermal desorption equipment.

3. Mass Spectrometer

- Mass spectrometer interfaced to the above gas chromatograph and to a data system with capabilities conforming to the specifications given in Method 624 Part 4.9 which appears in Section 7.4 of this Appendix.
- Magnetic tape storage capability
- NIH/EPA library
- Software with a minimum capability of real-time acquisition of data, data manipulation and library searching.

C. Analytical Procedure

Tenax cartridges from the Love Canal area are to be analyzed in numerical order based on the sample ID numbers assigned by the Sample Bank at Niagara Falls. In addition, care must be taken to desorb the cartridges in the opposite direction of sampling flow. The sampling inlet end is identified by two glass wool plugs; desorption will be performed using opposite flow (i.e., connecting desorption unit inlet to single plug end).

Before initiation of sample analysis, a 3-point calibration curve is run in triplicate using standard Tenax cartridges.

The Tenax cartridges are analyzed by thermal desorption at 250°C for 10 minutes in an appropriate thermal desorption system. The desorbed organics are cryogenically trapped and subsequently flashed onto the glass capillary column specified below. The effluent from the capillary will be directly introduced into the mass spectrometer for analysis. The thermal desorption system should be operated according to the manufacturer's recommendations in order to accomplish this desorption.

The following gas chromatographic conditions are sufficient for analysis:

Column: 50M Chrompack, or equivalent, SE-30 thick phase, wide bore, WCOT, 0.5 mm ID glass capillary column (with film thickness 0.8-1.0 μm)

Injector temperarure: 200°C

Column Oven Conditions:

Initial: 25°C, hold 5 minutes
Ramp: 4°C/minute
Final: 200°C, hold 15 minutes

Approximate Flow: 2 cc/minute

Other column conditions may be used subject to the prior approval of the Technical Monitor.

The mass spectrometer must be operated to accommodate the narrow peak widths produced by the capillary column. The following mass spectrometer conditions are considered adequate for this purpose:

Source temperature: 250°C or normal EI operation temperature

Source pressure: $<4 \times 10^{-6}$ torr

Scan time: $\leq$ 1 sec

Mass range: 40 to 300 amu

Electron energy: 70 eV

Other operating conditions may be used subject to the prior approval of the Technical Monitor.

The concentrations (ng per tube) of the compounds designated for quantitation are determined by comparing their responses to the calibration curve. The minimum quantifiable limit is determined to be 50 ng per compound per tube. Each laboratory will define its limit of detection for each component to be identified as a signal to noise ratio of 4 to 1 and report this value in ng per tube. Components present at concentrations between this minimum detection limit and the minimum quantifiable limit are to be reported as "trace." The compounds designated for qualitative analysis should be reported as "present" or "not detected" as appropriate. In addition all spectra collected are to be archived on magnetic tape in the specified format.

1.2.2 Quality Control Procedures

Quality Control procedures to be followed in this analysis are described below. Included are the requirements for instrument calibration and the frequency and type of internal QC samples to be run. Each activity is described in some detail with references to standard methods made where appropriate. In addition, the control limits and corrective action for each activity are summarized in Table 1-1.

A. Tuning of Mass Spectrometer

Procedures for tuning of the GC/MS consist of injection of 50 ng of the standard reference compounds 4-Bromofluorobenzene and/or decafluorotriphenylphosphine (DFTPP) daily prior to the analysis of samples. Criteria to be met by DFTPP are given in Method 624; those for BFB are given below:

4-Bromofluorobenzene Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15-40% of the base peak
75	30-60% of the base peak
95	base peak, 100% relative abundance
96	5-9% of the base peak
173	less than 1% of the base peak
174	greater than 50% of the base peak
175	5-9% of mass 174
176	greater than 50% of the base peak
176	greater than 94% but less than 100% of 174
177	5-9% of mass 176

B. Calibration of GC/MS System

The GC/MS system must be initially calibrated to determine response factors by generating a 3-point calibration curve in triplicate. After the system has been calibrated, the calibration for organic compounds must be verified at least once each day of running (8 hours) by the use of standard Tenax cartridges. If the deviation from actual concentration is greater than 20 percent, the system must be recalibrated. Information regarding the verification of calibration should be recorded and provided to the Prime Contractor.

C. Internal Standard

At the option of the analyst, an internal standard of hexafluorobenzene may be spiked onto each standard, blank, and sample Tenax cartridge. This internal standard is not required and its use depends primarily on the availability of the apparatus needed to perform such spiking.

TABLE 1-1. INTERNAL QC REQUIREMENTS - VOLATILE ORGANICS ON TENAX

Operation check	Frequency	Control limits	Corrective action planned
Tuning of mass spectrometer	Daily prior to analysis of samples	As specified in text	Retune spectrometer
Verify capillary column performance	Daily prior to analysis of samples	As specified in text	Check analytical procedure Analyze second reference sample Replace column
Internal standard	Optional addition to every sample	Not required	Check analytical procedure Analyze reference sample Invalidate results and recalibrate
Method blank	One per 8 hours of analysis time After sample with heavy organic loading	No significant concentrations found	Check analytical procedure Analyze reference standard Invalidate results
Check thermal desorption system	Once per 8 hours of analysis time	To be determined	Adjust to appropriate levels Verify analytical results obtained while flows or temperature were incorrect
Laboratory control standard (LCS) - also serves as calibration check	One during first half of each 8 hours of analysis time	Deviation less than 20 percent of actual concentration	Check analytical procedure Analyze second reference sample Invalidate results and generate new standard curve

D. Capillary Column Performance

Capillary column performance will be monitored with "Grob" (acetophenone, 2,6-dimethylphenol, 2,6-dimethylaniline, nonanone, ethyl benzene and para-xylene) mixture spiked onto calibration and quality control checking cartridges. The adequacy of the column(s) to be used should be determined initially by injection of this Grob (or similar) mixture by GC/FID. The criteria for monitoring the performance of the column in the thermal desorption mode and the minimum requirements are as follows:

(1) RESOLUTION $= \frac{2(W_1 - W_2)}{W_1 - W_2} < 1.20$

where W_1 = Average base width of ethylbenzene measured at the base

W_2 = Average base width of p-xylene measured at the base

(2) PERCENT PEAK ASYMMETRY FACTOR (PAF) $\% \text{ PAF} = \frac{B}{F} \times 100$

where B = Area of back half of peak

F = Area of front half of peak

Both measured at 10 percent above baseline

% PAF for acetophenone <260

% PAF for nonanone <130

These criteria do not apply to cases in which "frontal tailing" and/or frontal shoulders are apparent. These situations, where F is greater than B, are highly unlikely to occur and must be evaluated on an individual basis.

(3) ACIDITY TEST (A.T.) = 1 ± 0.1 $\text{A.T.} = \frac{\text{PAWB}}{\text{PAA}}$

where PAWB = Peak area of dimethylaniline

PAA = Peak area of acetophenone

(4) BASICITY TEST (B.T.) = 0.8 ± 0.03 $\text{B.T.} = \frac{\text{PAWA}}{\text{PAA}}$

where PAWA = Peak area of dimethylphenol

PAA = Peak area of acetophenone

E. Thermal Desoprtion System Check

Proper operating temperatures and gas flow rates for the thermal desorption system must be verified for every 8 hours of analysis time.

F. Laboratory Control Standards (LCS)

Laboratory control standards (LCS) will be employed to identify systematic method and operator errors. For these analyses, the compounds to be quantitatively identified are spiked onto Tenax cartridges for use as the LCS. These standard cartridges are provided by the Prime Contractor. One LCS must be run during the first half of every 8 hours of analysis. The measured concentration for each compound in the LCS must be within 20 percent of the actual concentration.

G. Method Blanks

One method blank (blank Tenax cartridge) must be processed during each 8 hours of analysis time. In addition, a blank cartridge is to be run after analysis of a sample exhibiting heavy organic loading. A log should be maintained of the order in which blank cartridges are run. The method blank must not show any signals corresponding to compounds being measured on Tenax in the Love Canal Study.

1.3 PESTICIDES AND RELATED COMPOUNDS ON POLYURETHANE FOAM PLUGS

1.3.1 Analytical Procedures

A number of pesticides and related compounds are monitored in the Love Canal area using polyurethane foam plugs for collection of ambient air. The organic compounds of interest are listed below:

Quantitative Analysis

- Lindane
- Hexachlorobenzene
- Hexachlorocyclopentadiene
- 1,2,3,4-Tetrachlorobenzene
- 1,2,3-Trichlorobenzene
- 1,2,4-Trichlorobenzene
- 1,3,5-Trichlorobenzene
- 2,4,5-Trichlorophenol
- Pentachlorobenzene

Qualitative Analysis

- Hexachloro-1,3-butadiene
- 1,2,4,5-Tetrachlorobenzene
- α,α,2,6-Tetrachlorotoluene
- Pentachloro-1,3-butadiene
- Pentachloronitrobenzene
- 1,2,3,5-Tetrachlorobenzene
- α-Benzenehexachloride (α-BHC)
- Heptachlor

Polyurethane foam plugs are Soxhlet extracted with 5 percent ether in hexane. Chlorinated pesticides and PCBs are measured by electron capture-gas chromatography (EC-GC) after column chromatographic cleanup. Chlorinated phenols are quantified by EC-GC and/or HPLC without preliminary cleanup. Using the procedure described below, each sample will be analyzed by gas chromatography. Mass spectrometric confirmation will be conducted on composited and/or selected samples. Data are reported as nanograms (ng) per whole foam plug.

A. Sample Handling and Preservation

Polyurethane foam plugs for pesticide analysis are received by the laboratory according to chain-of-custody procedures. Internal chain-of-custody must be maintained. As received, the foam plug samples should be enclosed in the glass sampling module and should have been wrapped in hexane-rinsed aluminum foil. They should be maintained in this condition until time for analysis. Storage should be at 4°C.

B. Apparatus

- Gas chromatography equipped with linearized ^{63}Ni detector or equivalent detector.
- HPLC equipped with an electrochemical detector.
- Rotary vacuum evaporator.
- Centrifuge tubes, graduated, 12-15 ml.
- N-evap® apparatus (or equivalent) for evaporation of solvent under a gently nitrogen stream.
- Extractor, Soxhlet, 125, 250, or 500 ml.
- Cleanup microcolumn, Chromaflex® column, size 22, 20 cm x 7 mm (Kontes®) or equivalent.
- Chromatoflo® chromatography column, or equivalent, that can be operated under nitrogen pressure.
- Pasteur Pipettes (9").

C. Reagents

- Solvents, glass distilled, pesticide quality or equivalent.
- Standards, 98-100 percent pure, obtainable from Quality Assurance Section, U.S. Environmental Protection Agency, ETD, HERL, MD-69, Research Triangle Park, NC 27711.
- Alumina, basic, 60 mesh, Alfa Products®, or equivalent. Adjust to Brockmann activity IV by adding 6 percent (w/w) distilled water to the adsorbent in the flask, stoppering, and shaking well. Allow to equilibrate for at least 15 hours before use. Discard after 2 weeks.
- Nitrogen gas, dry, purified.

- Silicic acid, Mallinckrodt AR, 100 mesh; heat at 130°C for at least 7 hours and then cool to room temperature in a desiccator; deactivate as follows: weigh into a bottle, add 3 percent (w/w) distilled water, seal tightly, shake well and place in a desiccator for at least 15 hours. Discard any remaining after 1 week.

D. Extraction

After sampling, the foam plug in the glass module should have been wrapped in hexane-rinsed aluminum foil until analysis.

- Remove the foam plug with forceps and place into Soxhlet extractors.
- Extract with an appropriate volume of 5 percent ether in hexane for 50-100 cycles in the extractor.
- Remove the boiling flask to a rotary evaporator and reduce the solvent volume to approximately 5 ml. (CAUTION: Do not let sample go dry.)
- Transfer the concentrate to a graduated centrifuge tube with rinsing and adjust volume to exactly 10 ml.
- Pipette one-half of the sample into a second centrifuge tube. Use this half of the sample for determination of chlorinated phenols.

E. Determination of Organochlorine Pesticides and PCBs

- Reduce the volume in one of the centrifuge tubes to just below 1 ml by careful evaporation under a gentle stream of nitrogen at room temperature
- Carry out alumina cleanup as follows:
    - Place a small plug of pre-extracted glass wool in the Chromaflex column and wash with 10 ml of hexane, which is then discarded.
    - Pack the column with 10 cm of activity grade IV alumina.
    - Transfer the sample from the centrifuge tube to the top of the column; rinse the tube three times with successive 1 ml portions of _n_-hexane, adding and eluting each rinse into the column.
    - Add 15 ml of _n_-hexane and elute the column, collecting the eluate in a 15 ml centrifuge tube.

  - Adjust the final volume of the eluate by N_2 evaporation to 10 ml for gas chromatographic analysis.

- When necessary, separate PCBs from technical chlordane (which is found in nearly all homes) and other pesticides by silicic acid chromatography as follows:

  - Place 3 grams of deactivated silicic acid in a Chromatoflo column assembly.

  - Wash the column with hexane (CAUTION: Do not allow solvent level to go below the top of the silicic acid in the column.)

  - Place the sample, concentrated to less than 1 ml, on the column with a disposable Pasteur pipette.

  - Add 130 ml of hexane to the reservoir.

  - Apply nitrogen pressure to the column to increase the flow rate to ca. 1 ml/minute.

  - Collect three fractions in glass stoppered graduated cylinders: Fraction I (0-30 ml contains all the HCB and Aroclor 1254 and most of the Aroclor 1242; Fraction II (31-50 ml) contains the remainder of Aroclor 1242 and the early eluting peaks of technical chlordane; Fraction III (51-130 ml) contains the remainder of the technical chlordane, including all of the cis- and trans-chlordane.

  - Elute the remaining pesticides with 15 ml of dichloromethane,* which is added when the hexane level reaches the top of the silicic acid.

  - Adjust the fraction volumes and analyze by GC.

F. Gas Chromatography of Organochlorine Pesticides

- Determine all compounds except the chlorinated phenols on 180 cm x 4 mm I.D. glass columns packed with 1.5 percent OV-17/1.95 percent OV-210 and 4 percent SE-30/6 percent OV-210. The nitrogen flow should be 65-85 ml/minute. The analyses will have to be carried out at both low and high column temperatures (approximately 150° and 200°) in order to separate and characterize the broad range of compounds being sought.

---

*NOTE: Be careful to replace dichloromethane with hexane or iso-octane (2,2,4-trimethylpentane) before injecting on EC-GC.

- Inject 5 µl, or other appropriate volume, of the sample extract or cleanup column eluate into the gas chromatograph.

- Record chromatograms and measure retention times relative to aldrin or another suitable reference standard.

- Compare the retention time of each component of interest against those of the corresponding primary standard.

- Quantify components in the usual way; i.e., by measuring peak heights to the nearest mm when the base width is <1 cm or via peak areas by integration or triangulation for broader peaks.

- Confirm results as required by combined GC/MS (Method 625, Section 7.5 of this Appendix) or some other appropriate procedures (EPA Pesticide Analytical Quality Control Manual, Chapter 8).

- Quantify PCB mixtures by comparison of the total heights or areas of GC peaks with the corresponding peaks in the best-matching standard. Use Aroclor 1242 for early-eluting and either Aroclor 1254 or Aroclor 1260 as appropriate for late-eluting PCBs.

G. Determination of Chlorinated Phenols

- Determine di-, tri-, tetra-, and pentachlorophenols by EC-GC using a 0.6 m x 4 mm i.d. double support-bonded diethylene glycol succinate column (DSB-DEGS). Carrier gas - 5 percent methane in argon, flow 60 ml/min with an oven temperature of 145°C for di- and trichlorophenol and an oven temperature of 180°C for tetra- and pentachlorophenols.

  DSB-DEGS can be made following the method of Edgerton and Moseman[1] and Moseman.[2] This procedure is summarized in Part H below.

- All the chlorinated phenols may be analyzed by HPLC using an electrochemical detector. A Zorbax C8 column is utilized. The appropriate analytical procedure for determination of chlorophenols in human and environmental samples begins on page 7 of this section (1.3.1).

H. Preparation of Double Support Bonded-Diethylene Glycol Succinate (DSB-DEGS) Support:

- Place Chromosorb W, 80/100 mesh nonacid washed in a 350 ml Buchner funnel.

Acid wash the support by slurrying, in the funnel, with hot 6N HCℓ.

Draw off the acid using vacuum from a water aspirator.

Repeat the washing three to five times or until no traces of yellow color remain.

Wash the support with several rinsings of distilled water and then dry at 100°C overnight.

- Screen the support through 80/100 mesh ASTME-11 specification stainless steel screen to remove fines.

  Coat with the liquid phase (5%), in this case, diethylene glycol succinate (DEGS), using rotary evaporation until a uniform coating is achieved.

- Heat treatment or support bonding is accomplished in a Guild column conditioning oven at 270 to 280°C overnight.

  Double support bonding (DSB) is accomplished by coating an additional 5% of the DEGS liquid phase and heat treating again.

Analytical Methodology for the Determination of Chlorophenols in Human and Environmental Samples

EPA Report No. 600/2-80-181

Analytical Chemistry Branch
Environmental Toxicology Division
Health Effects Research Laboratory
Research Triangle Park, NC 27711

August 27, 1980

Methodology is presented for the determination of chlorophenols in human and environmental media. The methodology for air samples is a modification of the analysis of chlorophenols in blood and has not been fully investigated as to quantitative reliability.

Instrumentation Required

The liquid chromatographic system consists of a Tracor model 995 isochromatographic pump with a model CV-1-UHPa-HC Valco valve and a model LC-2A electrochemical detector from Bioanalytical Systems. The electrochemical detector is operated at an oxidation potential of +1.1 V. The electrode used is either carbon paste or glassy carbon. Zorbax® C8 columns of 15 or 25 cm length are used. Two different mobile phases must be used to determine all chlorophenol congeners since gradient elution cannot be used with the electrochemical detector.

The mobile phase used for the early eluting phenols is 46% 0.05 M, pH 4.0 phosphate buffer, 40% methanol, 14% acetonitrile. The mobile phase used for the later eluting phenols is 50% phosphate buffer, 50% acetonitrile. All solvents are chromatographic grade and are filtered through 0.4 micron filters before use. All necessary phenol standards can be obtained from Aldrich Chemical Co.

Analysis of Urine Samples

The samples are prepared for analysis by the method of Edgerton et al.[1] Briefly, a 4 mL aliquot of urine is placed in a 15-mm x 125-mm screw cap culture tube, 1 mL of concentrated hydrochloric acid is added, and the tube is heated in a boiling water bath for one hour. The hydrolyzed urine is tranferred to a XAD-4 macroreticular resin column. After several aqueous washes, the chlorinated phenols are eluted with 10% 2-propanol in hexane. This eluant is concentrated to appropriate volumes and analyzed by EC-GC and by electrochemically detected HPLC. The organic solvent extract containing the chlorinated phenols from the above method is partitioned with 0.1 N NaOH. The volume of 0.1 N NaOH is equal to the volume of the original urine sample. The aqueous layer containing the phenols is transferred to a 13 ml graduated centrifuge tube and acidified with concentrated H_3PO_4 to a pH of 3 to 4 as determined with pHydrion paper. An aliquot from the aqueous phase is then injected into the liquid chromatograph.

Analysis of Blood Samples

The method reported by Lores, et al.[2] for the determination of halogenated anilines in urine by high-performance liquid chromatography with an electrochemical detector (HPLC/ECD) is modified and used for analysis of chlorophenol residues in blood. Whole blood samples (3-7 g) are hydrolyzed in dilute hydrochloric acid solution before the phenolic compounds are extracted into 1:1 (v/v) hexane/ethyl ether. The organic extracts are then partitioned with sodium hydroxide solution and the aqueous alkaline solutions containing the phenols are buffered by addition of phosphoric acid (amount dependent upon concentration of chlorophenols anticipated) before portions are analyzed by HPLC/ECD under isocratic elution conditions.

The response and instrumental noise level of the electrochemical detector varied slightly from day to day so that a fixed limit of measurement cannot be quoted for the method. Instead, the limit of detection for the instrument is defined as the response of each phenol analyzed required to produce a signal to noise ratio of five; usually it is at 5 ng injected.

Phenol and 2-chlorophenol (2-CP) cannot be analyzed using this method. Fortification-recovery experiments are shown in Table 1.

Analysis of Air Samples

The method for the determination of chlorophenols in blood by HPLC/ECD is modified and used for analysis of chlorophenol residues in air. Polyether-type polyurethane foam is used to collect air samples according to Environmental Protection Agency "Protocol for Assessment of Human Exposure to Airborne Pesticides.[3] The methods for chlorophenols involve the following steps:

1. Remove the foam plug with forceps and place into Soxhlet extractors.
2. Extract with an appropriate volume of 5% diethyl ether (stabilized with 2% ethanol, Mallinkrodt 0850) in hexane for 50-100 cycles in the extractor.
3. Remove the boiling flask to a rotary evaporator and reduce the solvent volume to approximately 5 mL. (CAUTION: Do not let sample go dry.)
4. Transfer the concentrate to a graduated centrifuge tube with rinsing and concentrate volume to exactly 2mL.
5. Partition the extract into appropriate volumes of 0.1 N aqueous sodium hydroxide, which when buffered with phosphoric acid will permit maximum detectability of chlorophenols.
6. Analyze buffered solution according to the procedure described above.

Table 1. Recoveries of Chlorophenal Standards Added to Whole Blood[a]

Sample	3-CP	4-CP	2,4-DCP	2,4,6-TCP	2,4,5-TCP	PCP
ACB pooled blood	-[b]	-	-	-	-	3[c]
ACB pooled blood, low level fortification amounts						
found 1	36.2	44.2	47.3	36.2	52.6	80.0
2	38.4	41.7	38.4	39.3	55.7	97.8
3	42.3	48.3	46.5	34.5	46.9	56.6
4	42.2	47.1	44.4	36.4	44.4	76.8
5	43.7	36.7	46.2	38.2	52.2	115
Average amount found	40.6	43.6	44.6	36.9	50.4	85.3
Amount added	50.7	44.8	47.2	45.2	50.4	105
Average percent recovery	80	97	94	82	100	81
RSD[d]	6.2	11	8.1	5.1	9.1	26
ACB pooled blood, high level fortification amounts						
found 1	450	380	425	346	400	1008
2	460	380	450	345	460	760
3	649	428	428	391	438	695
4	447	408	384	384	413	549
5	440	419	393	419	450	1013
Average amount found	489	403	416	377	432	805
Amount added	507	448	472	452	504	1050
Average percent recovery	96	90	88	83	86	77
RSD	18	5.5	6.5	8.4	5.8	25
Overall average percent recovery (N=10)	88	94	91	83	93	79
RSD	17	9.2	7.9	6.7	11	24

[a] Fortified blood samples weighed from 4.5 to 5.5 g and the amounts of chlorophenols added and found are given in ng.

[b] A dash indicates not present at the limit of detection for the method which was set at a signal to noise ratio of 4.

[c] This value was used to correct the amounts found.

[d] RSD = relative standard deviation (coefficient of variation).

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1. T. R. Edgerton, R. F. Moseman, E. M. Lores, and L. H. Wright, *Anal. Chem.*, in press (1980).

2. E. M. Lores, F. C. Meekins, and R. F. Moseman, *J. Chromatogr.*, *188*, 412-416 (1980).

3. R. G. Lewis, M. D. Jackson and K. E. MacLeod, "Protocol for Assessment of Human Exposure to Airborne Pesticides," U. S. Environmental Protection Agency Report, EPA 600/2-80-180 (1980).

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1. T. R. Edgerton and R. F. Moseman, Journal of Chromatographic Science, 18, 25-29 (1980).

2. R. F. Moseman, Journal of Chromatography, 166, 397-402 (1978).

1.3.2 Quality Control Procedures

The Quality Control procedures to be utilized in the analysis of polyurethane foam plugs are described in some detail below. These are the minimum internal QC requirements to be performed. The frequency, control limits, and corrective action for each activity are summarized in Table 1-2.

A. Standardization and Calibration

Procedures for the required calibration of the instrument for the analysis of pesticides extracted from foam plugs consist of the following points:

- A 3-point calibration curve of all compounds to be quantified must be generated each morning before any samples are run. Stock solutions for calibration standards are supplied by EPA-HERL/RTP.

- The calibration curve must be verified after every 5 samples analyzed by injecting a single concentration of the calibration mixture. If, for any of the compounds, the deviation from the actual concentration is greater than ±6 percent, then the entire calibration curve must be regenerated. All samples analyzed between the last acceptable calibration check and the check which failed to meet this criterion must be reanalyzed using the new calibration curve.

- If a suitable compound can be determined, a single internal standard will be added to each sample extract. This internal standard will serve to monitor instrument response between calibration checks.

- The instrument sensitivity must be checked whenever the calibration curve is checked. This is done by examining the Lindane component of the calibration mixture. The criterion to be met for instrument sensitivity is that the Lindane component must show half of full scale deflection for 225 picograms of that compound.

- The detection limit for these analyses is required to be 45 nanograms per whole plug extract. The quantifiable lower limit must be 90 nanograms per whole plug extract.

- A standard mixture of the compounds to be identified qualitatively must be injected after every 10 samples analyzed to monitor retention times of those compounds. The concentration of this mixed standard is left to the discretion of the subcontracting laboratory.

TABLE 1-2. INTERNAL QC REQUIREMENTS - POLYURETHANE FOAM PLUGS

Operation check	Frequency	Control limits	Corrective action planned
Calibration of instrument	Daily before analysis of samples	Not applicable	Not applicable
Calibration check	One after every 5 samples	Deviation less than ±6 percent	Check analytical procedure Analyze second reference standard Invalidate results and generate fresh standard curve
Sensitivity check	With calibration check	Lindane (225 pg) giving half of full scale deflection	Adjust to appropriate level Recalibrate as necessary
Qualitative compound standard check	After every 10 samples	Detection limits of 45 ng/plug or better	Check analytical procedure Recalibrate instrument
Laboratory control standard (LCS)	One per analysis batch[a]/ analysis day	To be determined	Check analytical procedure Analyze second reference sample Invalidate results
Method blank	One per analysis batch[a]/ analysis day	No significant concentrations found	Correct for blank Check analytical procedure

[a] Analysis batch = group of samples processed as a set, usually containing 15 samples or less.

B. Laboratory Control Standards (LCS)

Laboratory control standards (LCS) are employed to identify systematic method and operator errors. The LCS is a mixture of a number of compounds of known concentration in a reference material or spiked into reagent water. In this case, the standard mixture will be spiked onto blank foam plugs provided by the Prime Contractor. The concentration should be in the range of 250-400 nanograms per whole plug. Due to the lack of data is this area, acceptable recovery levels will be determined over the course of the program.

One LCS must be processed through the entire analytical method for each set of samples extracted in a group at the same time on the same day. Normally there will be one LCS for every 5-15 samples depending on how many samples are extracted in a given batch.

Stock standard materials for preparing the LCS will be provided by Mr. Randall Watts, Quality Assurance Section, U.S. EPA, HERL/RTP. Each of the compounds will be provided from the same lot. The minimum required compounds to be used in the LCS are as follows:

Lindane

Hexachlorobenzene

Hexachlorocyclopentadiene

1,2,3,4-Tetrachlorobenzene

1,2,3-Trichlorobenzene

1,2,4-Trichlorobenzene

1,3,5-Trichlorobenzene

2,4,5-Trichlorophenol

Pentachlorobenzene

C. Method Blanks

One method blank (blank foam plug) must be processed through the entire laboratory analytical procedure for each set of samples extracted in a group at the same time on the same day. Normally this will be one method blank for every 5-15 samples depending on how many samples are extracted in a given batch. The method blank must not show any signals that correspond to compounds on the Love Canal or priority pollutants list. If common laboratory contaminants are found in the method blanks, reported values for the same compounds in the environmental samples must be reduced by the amount found in the blank.

D. Replicate Analyses

Due to the nature of the polyurethane foam plug samples, it is not possible to perform replicate extractions and analyses as part of internal Quality Control.

1.4 METALS

1.4.1 Analytical Procedures

Metals in ambient air will be determined by collection on high volume (hi-vol) filters and subsequent elemental analysis after appropriate sample preparation. The metals to be quantified are the following:

- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Chromium
- Copper
- Lead
- Mercury
- Nickel
- Selenium
- Silver
- Thallium
- Zinc

The analysis of metals on hi-vol filters is performed using the procedures presented in this section. Quality control procedures are described in Section 1.4.2 of this Appendix.

ICP-OES PROCEDURE FOR DETERMINING TRACE ELEMENTS IN SUSPENDED PARTICULATE MATTER COLLECTED ON GLASS FIBER FILTERS

(1980 NAMS PROCEDURE)

JULY 8, 1980

ENVIRONMENTAL MONITORING DIVISION
ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N.C.

TABLE OF CONTENTS

1. Principle and Applicability Page 1
2. Ranges, Sensitivities and Lower Detectable Limits 1
3. Interferences 2
4. Precision and Bias 3
5. Apparatus 3
    5.1 Sampling 3
    5.2 Analysis 3
6. Reagents 5
    6.1 Sampling 5
    6.2 Analysis 7
    6.3 Master Calibration Standards 12
    6.4 Working Standards 34
    6.5 Instrumental Quality Control Solutions 34
7. Procedure 34
    7.1 Sampling 34
    7.2 Analysis 35
8. Calibration 40
9. Computations 41
    9.1 Real Time Judgments 41
    9.2 Post Analysis Judgments 44

Tables 47 ff.

OES PROCEDURE FOR DETERMINING TRACE ELEMENTS IN 1980 NAMS SAMPLES

1. Principle and Applicability

1.1 Ambient air suspended particulate matter is collected on a glass fiber filter for 24 hours using a High Volume sampler.

1.2 Trace elements in the particulate matter collected on the glass fiber filter are solubilized in a mixture of nitric acid and hydrochloric acids with the aid of heat and ultrasonication.

1.3 The trace element concentration of the nitric acid hydrochloric acid mixture is determined after diluting to the analytical instruments working range. The analytical instrument used by this laboratory is an inductively coupled plasma emission spectrometer. The operating parameters recommended by the instruments manufacturer are followed. The data output from the analytical instrument is processed by computer into micrograms of trace metals per cubic meter of air sampled.

2. Ranges, Sensitivities, and Lower Detectable Limits

2.1 Typical maximum concentrations for the inductively coupled plasma emission spectrometer used by this laboratory are given in Table 1.

2.2 Calibration Sensitivities. Sensitivities are dependent upon spectral line intensities. Typical sensitivities for the inductively coupled plasma emission spectrometer used in this laboratory are given in Table 2 in terms of output increment per µg of the element.

2.3 Instrumental Detection Limits. Typical detection limits achievable by the inductively coupled plasma emission spectrometer used in this laboratory are given in Table 3. These are computed as three (3) times the standard deviation of the distribution of outputs for the repeated measurement of Std. No. 1. The acid concentrations of this standard match the acid concentrations of blanks and samples. These data were obtained from 100 random determinations of Std. No. 1 (Zero Level) over a four week period.

3. Interferences

3.1 Spectral Interferences. Spectral interferences result where spectrally pure solutions of one element produce a finite output on channels assigned to other elements. When performing the quantitative correction, the order of correction is arranged so that only "true" (that is interference free or previously corrected) values are utilized in any quantitative correction of another element. Table 4 lists the quantitative correction factors in the order in which they were applied by the data processing step. The correction relation for any affected element is:

"True" conc = Apparent Conc - Factor ("True" conc affecting element).

3.2 Matrix Interferences. Matrix interferences do exist. The problem has been treated by matrix matching of standards and samples.

4. Precision and Bias

4.1 Accuracy is unknown for the entire procedure. Analysis of blind replicate samples treated as independent samples usually produce a coefficient of variation for an individual measurement of less than 20%.

5. Apparatus

5.1 Sampling.

5.1.1 High Volume Sampler. Use and calibrate the sampler as described in Reference 1.

5.2 Analysis.

5.2.1 Acid Digestion Bomb. (Parr 4745 or equivalent).

5.2.2 Centrifuge. Equipped with 8 place rotor and 30.2 x 100 mm shields. (Drucker 803 or equivalent).

5.2.3 Desiccator. For cooling oven-dried chemicals.

5.2.4 Drying Oven.

5.2.4.1 Gravity Convection Type. For drying chemicals and glassware. (Precision Scientific 31281 or equivalent).

5.2.4.2 Mechanical Convection Type. For drying plasticware. (Blue M OV 510A-2 or equivalent).

5.2.5 Gloves. Examination type, vinyl disposable, prepowdered, not sterilized. For personnel safety when handling particulate bearing glass fiber filters.

5.2.6 Hot Plate. (Corning 6795-35 or equivalent).

5.2.7 Hot Plate/Stirrer (Corning 6795-351 or equivalent).

5.2.8 Inductively Coupled Plasma Emission Spectrometer. (Jarrell-Ash Model 975 Plasma AtomComp). The instrument uses a Plasma-Therm HFS 2000D R.F. Generator as the power supply for the plasma. The excitation source is a three turn inductively coupled plasma torch with a cross flow pneumatic nebulizer for sample introduction. Samples are pumped to the nebulizer with a Gilson Minipuls II single channel peristaltic pump. The instrument is equipped to read 48 elements and an electronic internal standard. A dedicated PDP-8E (Digital Equip Corp) minicomputer controls the instrument and yields a concentration printout. To achieve data storage capability, the PDP-8 has been interfaced with a PDP-11/34.

5.2.9 Labware. Class A borosilicate glassware or where specified plasticware should be used.

5.2.9.1 Bottles. Linear polyethylene or polypropylene with leak-proof caps for storage of standards and samples. 500 ml, 125 ml and 30 ml are required. Teflon is used for storage of multielement standards.

5.2.9.2 Centrifuge Tubes. Polypropylene tube with screw tops of polypropylene, 50 ml volume (Nalgene 3119-0050).

5.2.9.3 Pipettes. For preparing standards and samples.

5.2.9.3.1 Pipettes. Volumetric 50 ml, 25 ml, 20 ml, 15 ml, 10 ml, 9 ml, 8 ml, 7 ml, 6 ml, 5 ml, 4 ml, 3 ml, 2 ml.

5.2.9.3.2 Pipette Graduated 10 ml.

5.2.9.3.3 Pipette Automatic Dispensing with accuracy of setting of 0.1 ml or better and repeatability of 20 µl (Grumman Automatic Dispensing Pipette, model ADP-30DT, or equivalent).

5.2.9.4 Cleaning. All labware should be scrupulously cleaned. The following procedure is recommended. Wash with laboratory detergent or ultrasonicate 30 minutes with laboratory detergent, rinse, soak a minimum of 4 hours in 20% V/V nitric acid, rinse three times with distilled deionized water, and oven dry.

5.2.9.5 Magnetic Stirrer with 25 mm Teflon-coated magnet (Corning 6795-353 or equivalent).

5.2.9.6 Pizza Cutter. Thin wheel. Thickness less than 1 mm.

5.2.9.7 Rack. For holding centrifuge tubes during ultrasonification.

5.2.9.8 Template. To aid in sectioning the glass fiber filter. See Reference 2, Figure 1 for dimensions.

5.2.9.9 Ultrasonic Bath. (Heat Systems Ultrasonic Inc. Model B92 H or equivalent). Cleaning power 425 watts, Heating power 400 watts.

5.2.9.10 Weighing Balance. Accurate to 0.1 mg or less.

6. Reagents

6.1 Sampling

6.1.1 Glass Fiber Filters Appropriate for Hi-Vol sampler.

6.1.1.1 Trace Metals Content. The absolute trace metals content of filters is not critical, but low values are desirable. It is important that the variation in extractable trace metals from filter to filter, within a batch, be small.

6.1.1.2 Discrimination Limit and Acceptance Testing.

6.1.1.2.1 Select at random 30 unexposed filters from the batch of filters used. Cut one 1-inch by 8-inch strip from each filter anywhere in the filter. Analyze all strips, separately, according to the directions in Sections 7 and 8.

Since individual blanks are not available from each filter used for sampling, the mean unexposed filter value is subtracted from each exposed sample's result to obtain the best estimate of each element in the filter particulate.

A limit of discrimination must be defined so that possible contributions from an individual filter are not falsely reported as being from the particulate.

6.1.1.2.2 Calculate the filter batch mean $\bar{M}_b$ and also the standard deviation from the M_b values for each filter. If $\bar{M}_b$ is less than the instrumental detection limit no correction for the element in the filter is necessary. If $\bar{M}_b$ is greater than the instrumental detection limit then $\bar{M}_b$ must be subtracted from the total elemental content from each particulate bearing filter when calculating the net metal in the particulate.

Determine the smallest atmospheric concentration of the element which can be reliably distinguished from the filter's contribution by multiplying the standard deviation for the filter batch by 3.3 and dividing by the average volume of air sampled, usually 2500 m^3.

$$L_D = \frac{3.3\ \sigma\ \text{blank}\ \mu g}{2500\ m^3} = \frac{\mu g}{m^3}$$

L_D = The discrimination limits smallest concentration of the element per cubic meter of air sampled which can be reliably distinguished from a possible false contribution of an individual filter. If L_D is unacceptably large then another batch of filters must be sought.

6.2 Analysis.

6.2.1 Acids.

6.2.1.1 Hydrochloric Acid.

6.2.1.1.1 Hydrochloric Acid, ACS reagent grade, concentrated (11.7N). For preparing standards and samples. (Fisher A-144 or equivalent).

6.2.1.1.2 Hydrochloric Acid, Ultrex grade (12.12N). For preparing standards. (Baker 1-4800 or equivalent).

6.2.1.2 Hydrofluoric Acid, ACS Reagent grade (49% W/W.). For preparing standards. (Fisher A-147 or equivalent).

6.2.1.3 Nitric Acid.

6.2.1.3.1 Nitric Acid, ACS Reagent grade concentrated (16N). For preparing 20% V/V nitric acid to clean labware only. This acid is not for sample preparation; it contains excessive metals. (Fisher A-200 or equivalent).

6.2.1.3.2 Nitric Acid, Redistilled Spectrographic grade (16N). For preparing samples. (Calvert Chemical spectrographic grade or equivalent).

6.2.1.3.3 Nitric Acid, Ultrex grade (15.95N) for preparing standards. (Baker 1-4801 or equivalent).

6.2.2 Aluminum Rod. Purity 99.995%. (Johnson Matthey JMC 340 or equivalent).

6.2.3 Ammonium Aquochlororuthenite. Purity 99.999%. (Johnson Matthey JMC 915 or equivalent).

6.2.4 Ammonium Chlororhodite. Purity 99.999%. (Johnson Matthey JMC 930 or equivalent).

6.2.5 Ammonium Dihydrogen Orthophosphate. Purity 99.999%. (Spex Industries Hi-pure or equivalent).

6.2.6 Ammonium Hexoflurosilicate. Purity 99.9999%. (Spex Industries Hi-pure or equivalent).

6.2.7 Antimony Powder. Purity 99.9999%. (Research Inorganic Chemicals SB-111 or equivalent).

6.2.8 Arsenic Trioxide. Purity 99.999%. (Johnson Matthey JMC 642 or equivalent).

6.2.9 Barium Carbonate. Purity 99.999%. (Johnson Matthey JMC 92 or equivalent).

6.2.10 Beryllium Flakes. Purity 99.95%. (Johnson Matthey JMC 110 or equivalent).

6.2.11 Bismuth Oxide. Purity 99.999%. (Spex Industries 1217 or equivalent).

6.2.12 Boron Powder. Purity 99.9%. (Spex Industries 1118 or equivalent).

6.2.13 Cadmium Rod. Purity 99.9999%. (Johnson Matthey JMC 170 or equivalent)

6.2.14 Calcium Carbonate. Purity 99.9999%. (Johnson Matthey JMC 90 or equivalent).

6.2.15 Cerium Oxide. Purity 99.988%. (Johnson Matthey JMC 304 or equivalent).

6.2.16 Chromium Pellets. Purity 99.999%. (Spex Industries 1122 or equivalent).

6.2.17 Cobalt Sponge. Purity 99.999%. (Spex Industries 1123 or equivalent).

6.2.18 Copper Powder. Purity 99.999%. (Johnson Matthey JMC 33 or equivalent).

6.2.19 Distilled Deionized Water. Distilled building water supply passed through a deionizer system. (Millipore Corporation Milli-Q or equivalent).

6.2.20 Extracting Acid. (2.23 M HCl, 1.03 M HNO_3). In a 1 liter volumetric flask, combine in order and mix well: 500 ml distilled deionized water, 64.6 ml concentrated (16 M) redistilled spectrographic grade nitric acid and 182.0 ml of ACS grade concentrated hydrochloric acid. Cool and dilute to 1 liter with distilled deionized water. Caution: Nitric Acid Fumes are Toxic. Prepare in a well ventilated fume hood.

6.2.21 Germanium Dioxide. Purity 99.9995%. (Johnson Matthey JMC 515 or equivalent).

6.2.22 Gold Sponge. Purity 99.9999%. (Johnson Matthey JMC 73 or equivalent).

6.2.23 Hydrogen Peroxide. 30% W/W. ACS Certified. (Fisher H-325 or equivalent).

6.2.24 Indium Oxide. Purity 99.999%. (Johnson Matthey JMC 385 or equivalent).

6.2.25 Iron Sponge. Purity 99.999%. (Johnson Matthey JMC 847 or equivalent).

6.2.26 Lanthanum Oxide. Purity 99.997%. (Johnson Matthey JMC 303 or equivalent).

6.2.27 Lead Nitrate. Purity 99.999%. (Johnson Matthey JMC 565 or equivalent).

6.2.28 Lithium Carbonate. Purity 99.999%. (Spex Industries 1234 or equivalent).

6.2.29 Magnesium crystals. Purity 99.998%. (Johnson Matthey JMC 126 or equivalent).

6.2.30 Manganese Dioxide. Purity 99.999%. (Johnson Matthey JMC 815 or equivalent).

6.2.31 Mercuric Oxide. Purity 99.9995%. (Johnson Matthey JMC 191 or equivalent).

6.2.32 Molybdenum Trioxide. Purity 99.998%. (Johnson Matthey JMC 726 or equivalent).

6.2.33 Nickel oxide. Purity 99.9999%. (Spex Industries 1239 or equivalent).

6.2.34 Niobium Powder. Purity 99.97%. (Johnson Matthey JMC 601 or equivalent).

6.2.35 Palladium Sponge. Purity 99.9995%. (Johnson Matthey JMC 940 or equivalent).

6.2.36 Platinum Sponge. Purity 99.999%. (Johnson Matthey JMC 1010 or equivalent).

6.2.37 Potassium Carbonate. Purity 99.999%. (Johnson Matthey JMC 17 or equivalent).

6.2.38 Rhenium Powder. Purity 99.999%. (Johnson Matthey JMC 830 or equivalent).

6.2.39 Samarium Oxide. Purity 99.9%. (Alfa Inorganics SM-102 or equivalent).

6.2.40 Selenium Dioxide. Purity 99.999%. (Johnson Matthey JMC 786 or equivalent).

6.2.41 Sodium Carbonate. Purity 99.999% (Johnson Matthey JMC 16 or equivalent).

6.2.42 Strontium Carbonate. Purity 99.998%. (Johnson Matthey JMC 91 or equivalent).

6.2.43 Tantalum Pentoxide. Purity 99.989%. (Johnson Matthey JMC 620 or equivalent).

6.2.44 Tellurium Dioxide. Purity 99.9995%. (Johnson Matthey JMC 798 or equivalent).

6.2.45 Thallium Oxide. Ultrapure grade. (Alfa Inorganics 78128 or equivalent).

6.2.46 Tin Shot. Purity 99.9999%. (Spex Industries 1158 or equivalent).

6.2.47 Titanium Sponge. Purity 99.9%. (Johnson Matthey JMC 431 or equivalent).

6.2.48 Tungsten Rod. Purity 99.99%. (Johnson Matthey JMC 740 or equivalent).

6.2.49 Vanadium Pentoxide. Purity 99.995%. (Johnson Matthey JMC 580 or equivalent).

6.2.50 Yttrium Oxide. Purity 99.975%. (Johnson Matthey JMC 301 or equivalent).

6.2.51 Zinc Splatters. Purity 99.999%. (Spex Industries 1163 or equivalent).

6.2.52 Zirconium Oxide. Spec. Grade. (Alfa Inorganics 81136 or equivalent).

6.3 Master Calibration Standards. Note: Individual single element master stock standards are prepared. Aliquots of these are then further diluted for individual use and/or mixed in compatible groups for more efficient multielement standardization of the spectrometer. The following section provides procedures for preparation of the stock standards. These are followed by instructions for preparing the five multielement working standards.

6.3.1. Master Standard, 5000 µg Al/ml. Dissolve 2.5000g of aluminum rod. (Johnson Matthey JMC 340 or equivalent) in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) by heating gently with a hot plate (Corning 6795-35 or equivalent). The dissolving process may take 10 days.

Add 300 ml of distilled deionized water and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Cool to room temperature; dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.2 Master Standard, 500 μg As/ml. Dissolve 0.33008 g of arsenic trioxide (Johnson Matthey JMC 642 or equivalent), that has been oven dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Stir and heat gently with a hot plate/stirrer (Corning 6795-351 or equivalent) for 24 hours to complete the dissolving process. Cool to room temperature; dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.3 Master Standard, 500 μg Au/ml. Dissolve 0.25000 g of gold sponge (Johnson Matthey JMC 73 or equivalent) in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 24 hours or longer for the dissolving process. Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.4. Master Standard, 1000 µg B/ml. Dissolve 0.50000 g of boron powder that has been oven dried overnight at 90 degrees Celsius and cooled in a desiccator in a 500 ml volumetric flask with 18.64 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Heat gently with a hot plate (Corning 6795-35 or equivalent) for 24 hours to dissolve the boron powder. Cool, then add 400 ml of distilled deionized water and 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.5 Master Standard, 1000 µg Ba/ml. Dissolve 0.71847 g of barium carbonate (Johnson Matthey JMC 92 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask by slowly adding 200 ml of standard No. 1 (page 52); Wait 4 hours for the dissolving process. Dilute to 500 ml with standard No.1 (page 52); stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or eouivalent).

6.3.6 Master Standard, 500 µg Be/ml. Dissolve 0.25000 g of beryllium flakes (Johnson Matthey JMC 110 or equivalent) in a 500 ml volumetric flask by slowly adding 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Allow 4 hours for completion of the dissolving process; then add 9.75 ml of Ultrex (15.95N) nitric acid (Baker 4801 or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene-1600-0016 or equivalent).

6.3.7 Master Standard, 1000 μg Bi/ml. Dissolve 0.55742 g of bismuth oxide (Spex 1217 or equivalent), that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 9.75 ml of Ultrex (15.95 N) nitric acid (Baker 1-4801) or equivalent) and 50 ml of distilled deionized water. Allow 4 hours for completion of the dissolving process. Dilute to 300 ml with distilled deionized water; add 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.8 Master Standard, 4000 μg Ca/ml. Dissolve 4.99448 g of calcium carbonate (Johnson Matthey JMC 90 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask by adding 200 ml of standard No.1(page 52). Allow 4 hours for completion of the dissolving process; dilute to 500 ml with standard No.1; stopper and invert the flask several times.

Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.9 Master Standard, 500 μg Cd/ml. Dissolve 0.25000 g of cadmium rod (Johnson Matthey JMC 170 or equivalent) in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Allow 24 hours for completion of the dissolving process. Add 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Dilute to 500 ml with distilled deionzied water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.10 Master Standard, 500 μg Ce/ml. Dissolve 0.30709 g of cerium oxide (Johnson Matthey JMC 304 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 30 ml of 30 percent hydrogen peroxide (Fisher H-325 or equivalent) and 19.50 ml of Ultrex (15.95 N) nitric acid (Baker 1-4801 or equivalent). Stir gently with a magnetic stirrer (Corning 699535 or equivalent) for 24 hours to complete the dissolving process; dilute to 500 ml with distilled deionized water; stopper and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent). Note: Hydrochloric acid will precipitate Ce, hence it was omitted from this standard.

6.3.11 Master Standard, 500 μg Co/ml. Dissolve 0.25000 g of cobalt sponge (Spex 1123 or equivalent) in a 500 ml volumetric flask with 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 4 hours for the dissolving process to go to completion. Add 400 ml of distilled deionized water and 27.59 ml of Ultrex (12.12N) hydrochloric acid, (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.12 Master Standard, 500 μg Cr/ml. Dissolve 0.25000 g of chromium pellets (Spex 1122 or equivalent) in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Allow 24 hours for the chromium to dissolve. Dilute to 400 ml with distilled deionized water. Add 9.75 ml of Ultrex (15.95 N) nitric acid (Baker 1-4801 or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.13. Master Standard 2000 μg Cu/ml. Note: The copper powder used to prepare this standard is received in 5.00000 g sealed glass vials so a copper super 50,000 μg/ml stock is prepared and diluted as needed for the master standard. For the super stock, dissolve 5.00000 g of copper powder (Johnson Matthey JMC 33 or equivalent) in a 100 ml volumetric flask by adding 10 ml of distilled deionized water and 48.75 ml of Ultrex (15.95 N) nitric acid (Baker 1-4801 or equivalent.) Allow 4 hours for the dissolving process to go to completion. Dilute to 100 ml with distilled deionized water. Stopper the flask and invert several times. Transfer this copper superstock to a clean labeled 125 ml teflon bottle (Nalgene 1600-0004 or equivalent). For the master standard, pipette 20 ml of copper super stock, 50.0000 mg Cu/ml, into a 500 ml volumetric flask. Add 400 ml of distilled deionized water and 27.59 ml of Ultrex (12.12 N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water. Stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.14 Master Standard, 5000 μg Fe/ml. Dissolve 2.50000 g of iron sponge (Johnson Matthey JMC 847 or equivalent), in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 8 hours for the iron to dissolve. Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times; transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.15 Master Standard, 500 μg Ge/ml. Dissolve 0.36020 g of germanium dioxide (Johnson Matthey JMC 515 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in the teflon cup of an acid digestion bomb (Parr 4745 or equivalent) with 10 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Close the bomb following the manufacturer's instructions and heat in an oven (Precision Scientific 31281 or equivalent) at 135 degrees Celsius for 5 hours. Allow the bomb to cool to room temperature. Quantitatively transfer the solution from the teflon cup of the bomb to a 500 ml volumetric flask. Add 17.59 ml of Ultrex (12.12N) hydrochloric acid. Dilute to 400 ml with distilled deionized water. Add 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801) or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.16 Master Standard, 500 µg Hg/ml. Dissolve 0.26994 g of mercuric oxide (Johnson Matthey JMC 191 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 19.50 ml Ultrex (15.95 N) nitric acid (Baker 1-4801 or equivalent). Allow 4 hours for completion of the dissolving process. Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent). Note: Hydrochloric acid will precipitate Hg, hence it was omitted from this standard.

6.3.17 Master Standard, 500 µg In/ml. Dissolve 0.30225 g of indium oxide (Johnson Matthey JMC 385 or equivalent), that has been oven-dried over night at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Stir gently with a magnetic stirrer (Corning 6795-35 or equivalent) for 24 hours to complete the dissolving process. Add 27.59 ml of Ultrex (12.12 N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water;

stopper the the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.18 Master Standard, 2000 µg K/ml. Dissolve 1.76734 g of potassium carbonate (Johnson Matthey JMC 17 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator in a 500 ml volumetric flask with 200 ml of distilled deionized water by slowly adding 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent) and 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Allow 4 hours for completion of the dissolving process. Dilute to 500 ml with distilled deionized water; stopper the flask, and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.19 Master Standard, 500 µg La/ml. Dissolve 0.29319g of lanthanum oxide (Johnson Matthey JMC 303 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator in a 500 ml volumetric flask with 9.75 ml of Ultrex (15.95 N) nitric acid (Baker 1-4801 or equivalent) and 50 ml of distilled deionized water. Allow 4 hours for completion of the dissolving process. Dilute to 400 ml with distilled deionized water; Add 27.59 ml of Ultrex (12.12 N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.20 Master Standard, 500 µg Li/ml. Dissolve 1.33102 g of lithium carbonate (Spex 1234 or equivalent), that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator in a 500 ml volumetric flask by slowly adding 200 ml of standard No.1 (Page 52). Allow 4 hours for the dissolving process to go to completion. Dilute to 500 ml with standard No. 1; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.21 Master Standard, 4000 µg Mg/ml. Dissolve 2.00000 g of magnesium crystals (Johnson Matthey JMC-126 or equivalent) in a 500 ml volumetric flask with 250 ml of standard No. 1 (page 52). Allow 24 hours for completion of the dissolving process. Dilute to 500 ml with standard No. 1 (page 52). Stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.22 Master Standard, 1000 µg Mn/ml. Dissolve 0.79123 g of manganese dioxide (Johnson Matthey JMC 815 or equivalent), that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95 N) nitric acid (Baker 1-4801 or equivalent). Stir and heat gently with a hot/plate stirrer (Corning 6795-351 or equivalent) for 48 hours to complete the dissolving process. Cool to room temperature and dilute to 500 ml with distilled deionized water. Stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.23 Master Standard, 500 µg Mo/ml. Dissolve 0.37507 g of molybdenum trioxide (Johnson Matthey JMC 726 or equivalent), that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, and 0.27540 g of undried ammonium carbonate (Fisher A-656 or equivalent) in a 500 ml volumetric flask with 400 ml of distilled deionized water by stirring vigorously with a magnetic stirrer (Corning 6795-353 or equivalent) for 48 hours. Add 9.75 ml of Ultrex (15.95 N) nitric acid (Baker 1-4801 or equivalent) and 27.59 ml of Ultrex (12.12 N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.24 Master Standard, 10,000 µg Na/ml. Dissolve 11.52565 g of sodium carbonate (Johnson Matthey JMC 16 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask by slowly adding 300 ml of standard No. 1 (page 52). Allow 4 hours for completion of the dissolving process. Dilute to 500 ml with standard No. 1; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.25 Master Standard, 500 μg Nb/ml. Dissolve 0.25000 g of niobium powder (Johnson Matthey JMC 601 or equivalent) in a 500 ml polymethylpentene volumetric flask (Nalgene 4001-0500 or equivalent) with 2 ml of 49% w/w hydrofluoric acid (Fisher A-147 or equivalent) by slowly adding 9.75 ml of Ultrex (15.95 N) nitric acid (Baker 1-4801 or equivalent). Allow 8 hours for the dissolving process to go to completion. Dilute to 400 ml with distilled deionized water, and add 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water; cap the flask tightly and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.26 Master Standard, 500 μg Ni/ml. Dissolve 0.31813 g of nickel oxide (Spex 1239 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95 N) nitric acid (Baker 1-4801 or equivalent). Stir and heat gently with a hot plate/stirrer (Corning 6795-351 or equivalent) for 48 hours. Cool to room temperature and dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.27 Master Standard, 2000 μg P/ml. Dissolve 3.71365 g of ammonium dihydrogen orthophosphate, that has been oven-dried 4 hours at 90 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) with 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 8 hours for the dissolving process to go to completion. Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.28 Master Standard, 2500 μg Pb/ml. Dissolve 1.99817 g of lead nitrate (Johnson Matthey JMC 565 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 19.50 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Stir for 24 hours with a magnetic stirrer (Corning 6795-353 or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent). Note: Hydrochloric acid will precipitate Pb, hence it was omitted from this standard.

6.3.29 Master Standard, 500 μg Pd/ml. Dissolve 0.25000 g of palladium sponge (Johnson Matthey JMC 940 or equivalent) in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 24 hours for completion of the dissolving process. Dilute to 500 ml with distilled deionized water. Stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.30 Master Standard, 500 µg Pt/ml. Dissolve 0.25000 g of platinum sponge (Johnson Matthey JMC 1010 or equivalent) in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 24 hours for completion of the dissolving process. Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.31 Master Standard, 1000 µg Re/ml. Note: The rhenium powder used to prepare this standard is received in 5.00000 g sealed glass vials so a rhenium super 50.000 mg/ml stock is prepared and diluted as needed for the master standard. For the super stock dissolve 5.00000 g of rhenium powder (Johnson Matthey JMC 830 or equivalent) in a 100 ml volumetric flask by slowly adding 50 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 4 hours for the dissolving process to go to completion. Dilute to 100 ml with distilled deionized water. Stopper the flask and invert several times. Transfer this rhenium super stock to a clean labeled 125 ml teflon bottle (Nalgene 1600-004 or equivalent). For the master standard, pipette 10 ml of this rhenium super stock, 50.000 mg/ml, into a 500 ml volumetric flask. Add 400 ml of distilled deionized water, 4.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent) and 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water. Stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.32 Master Standard, 500 µg Rh/ml. Dissolve 0.96390 g of ammonium chlororhodite (Johnson Matthey JMC 930 or equivalent), that has been oven-dried overnight at 95 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4800 or equivalent) and 25 ml of distilled deionized water. Heat gently with a hot plate (Corning 6795-35 or equivalent) for 8 hours to complete the dissolving process. Cool to room temperature. Add 400 ml of distilled deionized water and 27.59 ml Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water. Stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016) or equivalent).

6.3.33 Master Standard 1000 µg Ru/ml. Dissolve 1.64454 g of ammomium aquochlororuthenite (Johnson Matthey JMC 915 or equivalent), that has been oven-dried overnight at 88 degrees Celsius and cooled in a desiccator in a 500 ml volumetric flask with 250 ml of distilled deionized water, 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent) and 27.59 ml of Ultrex

(12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Allow 6 hours for the dissolving process to go to completion. Dilute to 500 ml with distilled deionized water. Stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.34 Master Standard, 500 µg Sb/ml. Dissolve 0.25000 g of antimony powder (Research Inorganic Chemicals SB-111 or equivalent) in a 500 ml polymethylpentene volumetric flask (Nalgene 4001-0500 or equivalent) with 2.0 ml of 49% w/w hydrofluoric acid (Fisher A-147 or equivalent) by slowly adding 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 12 hours for completion of the dissolving process. Add 250 ml of distilled deionized water and 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water. Cap the flask tightly and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.35 Master Standard, 500 µg Se/ml. Dissolve 0.35131 g of selenium dioxide (Johnson Matthey JMC 786 or equivalent), that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 100 ml of distilled deionized water and 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 4 hours for completion of the dissolving process. Dilute to 500 ml with distilled deionized water; stopper the flask, and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.36 Master Standard, 5000 μg Si/ml. Dissolve 15.85786 g of ammonium hexaflurosilicate (Spex Hi Pure or equivalent), that has been oven-dried 4 hours at 90 degrees Celsius and cooled in a desiccator, in a 500 ml polymethylpentene volumetric flask (Nalgene 4001-0500 or equivalent) with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent), 9.75 ml of Ultrex (15.95 N) nitric acid (Baker 1-4801 or equivalent), and 20 ml of distilled deionized water. Stir and warm gently for 4 hours to complete the dissolving process. Cool to room temperature and dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.37 Master Standard, 500 μg Sm/ml. Dissolve 0.28991 g of samarium oxide (Alfa Inorganics SM-102 or equivalent), that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Stir with a magnetic stirrer (Corning 6795-353 or equivalent) for 24 hours to complete the dissolving process. Dilute to 500 ml with distilled deionized water, stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.38 Master Standard, 500 μg Sn/ml. Dissolve 0.25000 g of tin shot (Spex 1158 or equivalent) in a 500 ml volumetric flask with 27.59

ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Stir and heat gently with a hot plate/stirrer (Corning 6795-351 or equivalent) for 72 hours to complete the dissolving process. Cool to room temperature; add 400 ml of distilled deionized water. While stirring, add 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.39 Master Standard, 500 μg Sr/ml. Dissolve 0.42122 g of strontium carbonate (Johnson Matthey JMC 91 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator in a 500 ml volumetric flask by slowly adding 250 ml of standard No. 1 (page 52). Allow 4 hours for completion of the dissolving process. Dilute to 500 ml with standard No. 1; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.40 Master Standard, 500 μg Ta/ml. Dissolve 0.30526 g of tantalum pentoxide (Johnson Matthey JMC 620 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator in the teflon cup of an acid digestion bomb (Parr 4745 or equivalent), with 2 ml of 49% w/w hydrofluoric acid (Fisher A-147 or equivalent). Close the bomb following the manufacturer's instructions and heat in an oven (Precision Scientific 31281 or equivalent) at 150 degrees Celsius for 5 hours. Allow the bomb to cool to room temperature. Place 300 ml of distilled deionized water, 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent) and 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) in a 500 ml polymethylpentene volumetric flask (Nalgene 4001-0500 or equivalent). Quantitatively transfer the solution from the teflon cup of the bomb to the volumetric flask. Dilute to 500 ml with distilled deionized water. Cap the flask tightly and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.41 Master Standard, 500 µg Te/ml. Dissolve 0.31269 g of tellurium dioxide (Johnson Matthey JMC 798 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent), 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent) and 50 ml of distilled deionized water. Stir with a magnetic stirrer (Corning 6795-353 or equivalent) for 12 hours to complete the dissolving process. Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.42 Master Standard, 500 µg Ti/ml. Dissolve 0.25000 g of titanium sponge (Johnson Matthey JMC 431 or equivalent) in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Allow 24 hours for completion of the dissolving process. Add 300 ml of distilled deionized water and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.43 Master Standard, 500 μg Tl/ml. Dissolve 0.27935 g of thallium oxide (Alfa Inorganics 78128 or equivalent), that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 24 hours for completion of the dissolving process. Dilute to 500 ml with distilled deionized water; stopper the flask, and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.44 Master Standard, 500 μg V/ml. Dissolve 0.44630 g of vanadium pentoxide (Johnson Matthey JMC 580 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric, flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 48 hours for completion of the dissolving process. Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.45 Master Standard, 500 μg W/ml. Dissolve 0.25000 g of chips from a tungsten rod (Johnson Matthey JMC 740 or equivalent) in a 500 ml polymethylpentene volumetric flask (Nalgene 4001-0500 or equivalent) with 2.0 ml of 49% w/w hydrofluoric acid (Fisher A-147 or equivalent) by slowly adding 2 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent). Allow 24 hours for completion of the dissolving process. Add an additional 7.75 ml of Ultrex (15.95 N) nitric acid. Dilute to 400 ml with distilled deionized water. Add 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.46 Master Standard, 500 µg Y/ml. Dissolve 0.31749 g of yttrium oxide (Johnson Matthey JMC 301 or equivalent) that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in a 500 ml volumetric flask with 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent) and 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801) or equivalent). Allow 24 hours for completion of the dissolving process. Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.47 Master Standard, 2000 µg Zn/ml. Dissolve 1.00000 g of zinc splatters (Spex 1163 or equivalent) in a 500 ml volumetric flask with 100 ml of distilled deionized water by adding 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent), and 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Allow 4 hours for completion of the dissolving process.

Dilute to 500 ml with distilled deionized water; stopper the flask and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.48 Master Standard, 500 μg Zr/ml. Dissolve 0.33770 g of zirconium oxide (Alfa Inorganics 86136 or equivalent), that has been oven-dried overnight at 110 degrees Celsius and cooled in a desiccator, in the teflon cup of an acid digestion bomb (Parr 4745 or equivalent) with 1.5 ml of 49% w/w hydrofluoric acid (Fisher A-147 or equivalent). Close the bomb following the manufacturers instructions and heat in an oven (Precision Scientific 31281 or equivalent) at 150 degrees Celsius for 5 hours. Allow the bomb to cool to room temperature. Open the acid digestion bomb and transfer the solution to a 500 ml polymethylpentene volumetric flask (Nalgene 4001-0500 or equivalent). Add 250 ml of distilled deionized water; 9.75 ml of Ultrex (15.95N) nitric acid (Baker 1-4801 or equivalent), and 27.59 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent). Dilute to 500 ml with distilled deionized water. Cap the flask tightly and invert several times. Transfer the solution to a clean labeled 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.3.49 Hydrochloric Acid 1.338N. Pipette 55.48 ml of Ultrex (12.12N) hydrochloric acid (Baker 1-4800 or equivalent into a 500 ml volumetric flask. Dilute to 500 ml with distilled deionized water. Stopper the flask and invert several times. Transfer the solution to a 500 ml teflon bottle (Nalgene 1600-0016 or equivalent).

6.4 Working Standards

Five working standards are required to standardize the ICP emission spectrometer. Element composition, aliquots of Sec.6.3 Master Standards required, and mixed concentrations are shown in Table 5. Prepare 2000 ml of Std. No. 1. This is used in preparation of the remaining standards. Add approximately 150 ml of Std. No. 1 to each of four 500 ml volumetric flasks. Add aliquots of Sec. 6.3 Master Standards as specified in Table 5. Bring each to volume with additional Std. No. 1, stopper, shake each thoroughly and transfer to teflon bottles and label.

6.5 Instrumental Quality Control Solutions

Two quality control solutions at different concentrations are used to assess, for the analyst, stability of the instrument calibration.

6.5.1 High QC. Prepare by adding approximately 500 ml of Std. No. 1 to a liter volumetric flask. Refer to Table 6 and pipette aliquots of Master calibration standards, Section 6.3 as indicated. Bring to volume with Std. No. 1, shake thoroughly and transfer to a teflon bottle. Most element concentrations are at 80% of the level in the working standards.

6.5.2 Low QC. Prepare 500 ml by adding about 200 ml of Std. No. 1 to a clean 500 ml volumetric flask. Pipette a 125 ml aliquot of high QC Sect. 6.5.1. Bring to volume with Std. No. 1, stopper, shake and transfer to teflon bottle.

7. Procedure

7.1 Sampling. Collect samples for 24 hours using the procedure described in Reference 1 with glass fiber filters. Transport collected samples to the laboratory taking care to minimize contamination and loss of sample.

7.2 Analysis

7.2.1 Sample Preparation. Cut a 1 inch by 8 inch strip from the 8 inch dimension of the folded particulate bearing filter using a template and a pizza cutter as described in Reference 2. Using vinyl gloves or plastic forceps accordion fold or tightly roll the filter strip and place it on its edge in a 50.0 ml screw top polypropylene centrifuge tube. Add 12.0 ml of extracting acid (6.2.18) using Channel A on the pre-set calibrated automatic dispensing pipette or with a regular pipette. (The acid should cover the strip completely.) Cap the tube loosely to prevent pressure build-up during the ultrasonication step. Place tube in a sample rack. Note: the sequence of adding the filter strip and acid to the centrifuge tube may be reversed, if more convenient, without affecting the results. Identify the sample by affixing a computer printed sample identification label to the centrifuge tube with tape. Put enough water, with a temperature of 100°C, in a clean ultrasonic bath so that the water level is slightly above the acid level of the centrifuge tubes in the rack. This water depth is well below the centrifuge tube caps and therefore prevents possible contamination of samples during ultrasonication. Set the loosely capped centrifuge tubes containing the samples and the extracting acid upright in the rack in the ultrasonic bath. It is important for the vials to be upright during the ultrasonication to prevent possible sample contamination.

Ultrasonicate the samples 50 minutes. Remove the centrifuge tubes containing the samples from the ultrasonic bath and blot the tubes dry. Uncap the centrifuge tube and add 28.0 ml of distilled deionized water to the tube using Channel B on the pre-set calibrated automatic dispensing pipette (two passes at 14.0 ml each), or with a regular pipette. Cap the centrifuge tube tightly and shake well. Place the tube in the centrifuge and centrifuge 20 minutes at 2500 rpm. Decant the clear solution from the centrifuge tube into an acid cleaned 30 ml polypropylene bottle (bearing sample ID label), taking care not to disturb the solids in the bottom of the tube. The sample is now ready for analysis. It has a 0.31 M nitric acid and a 0.67 M hydrochloric acid matric.

7.2.2 Determination

7.2.2.1 Jarrell Ash ICP Emission Spectrometer Operating Parameters.

Plasma Power	1.1 kw forward, automatic control. 11 W Reflected (minimum possible).
Argon Coolant	18 l/min. liquid argon source.
Aspiration argon	16 psi (app. 700 ml/min).
Sample Uptake	Avg. 1.78 ml/min.
Observation Zone	Centered 15 mm above the load coil.
Sample Preflush Time	45 seconds.
Preburn	1 Sec.
Exposure	10 Sec.
H_2O Post Flush	10 Sec.proceed to next sample.
Slits	25μ entrance slit; 75 μ exit slit.
Photomultiplier Tube Voltage	900 Volts

7.2.2.2 Jarrell-Ash ICP Standardization. Prepare the instrument as in 8.1.1. Profile following manufacturers directions. Open the standardization buffers with a "J" command on the CRT operating off-line from the PDP-11/34. Flush for two minutes with the first working standard. Make two exposures, print the average ratio on the teletype and identify the standard when queried. Repeat all five working standards. Complete with an "S" command and answer the query "Enter LCN" with a carriage return. Calibration data are not stored in the PDP-11.

7.2.2.3 Daily Operation of the ICP Spectrometer

1. Start and allow at least 45 minutes for warm up.
2. Profile and standardize according to 7.2.2.2.
3. Go on-line to the PDP-11 by typing RUN JA and answer PDP-11 queries to identify the operator, data storage and operating condition code.
4. The PDP-11 will automatically acquire Gains and Offsets determined by the ICP standardization. Sec. 7.2.2.2. These should be printed out on the teletype and examined for unusual values. Turn TTY off when complete.
5. Measure the sample pump uptake rate. This should be approximately 1.8 ml/min.
6. Select a QC sol'n for analysis. On the CRT enter; RTN (Return) 21 RTN for high QC, 22 RTN for low QC. When DESC: appears on CRT type HIQC or LOQC as applicable followed by its prep date, and RTN. The number 1.0 will appear twice indicating the multiplication and dilution factors have been set to 1.0. This is followed by the query "OK?"

7. Begin pumping from an aliquot of the QC solution selected in 6. Start the stopwatch when the leading edge of the solution has just entered the nebulizer. Time for 45 seconds, then press RTN on the CRT. This begins the exposure. The end is signaled by the CRT bell. Transfer the pickup tube to D.I. water.
8. When the PDP-11 has acquired the data it will query "QC SMP:" Type RTN and STD and 21 RTN. This identifies the Zero standard. After "DSC:" type the prep date of the zero std followed by RTN. As in 6 above, the multiplication and dilution factors will default to 1.0 and the query "OK" will appear.
9. Begin pumping from an aliquot of the zero standard and time for 45 seconds as in 7 above. Start the exposure with RTN on the CRT. At the bell return the pickup to D.I. water.
10. When the PDP-11 has acquired the data it will query "STD SMP:" Type 1, RTN, RTN and it will query "OK?" Type NO, RTN and the cursor will move to the left end of the line.
11. Select the first sample. Read the Project I.D. from the label and enter at the CRT. For 1980 NAMS this I.D. was N80 press RTN. Type numerical sample number and RTN. After "DSC:" Type the four letter I.D. code and RTN. The computer next queries "MLT:" for multiplication factor enter 360 RTN, followed by "DIL:" for dilution factor enter 1 RTN. The computer then asks "OK?"

12. Begin pumping sample from the sample bottle and time for 45 seconds before pressing RTN. At the bell return the pickup to D.I. water and select the next sample.
13. The second sample will be entered by typing the sample number, RTN, four letter I.D., RTN and the final RTN will begin the exposure.
14. Present eight samples to the instrument.
15. Challenge the instrument with the QC solution that was not selected in 6 above. Repeat steps 6 and 7 with respect to CRT entries and procedure.
16. Resume sample analysis. Repeat steps 11, 12 and 13.
17. Analyze nine samples.
18. Return to step 5 and repeat through step 17.
19. End the analytical session after about 3-3.5 hrs. Type -1 RTN. The computer will query "DO YOU WISH TO SAVE THIS SESSIONS DATA?" Type YES RTN. The computer will backup the data and issue instructions. This terminates the RUN JA program.
20. Usually two sessions per day are attempted. Repeat steps 2 through 19 for the second session.
21. Instrument operating parameters are recorded before and after every 20 burns. A typical days record is presented in Table 7.
22. With minimum experience the instrument operator will be able to compress the above steps, i.e. identify the sample being pumped, set aside the previous sample, select the following sample etc. and record instrument operating parameters.

8. Calibration

8.1 Preanalysis Investigation.

8.1.1 Calibration Curve Linearity. ICP spectrometers are generally considered to yield a linear response over wide concentration ranges. However, it is prudent to investigate for linearity, for elements expected to exceed concentrations of about 25 mg/l. This may vary among various manufacturers and according to operating parameters. The methods and conditions described in this procedure have imposed limitations as follows:

Ca linear to 40 mg/l, becoming non-linear
Cr saturates the electronics at 50 mg/l
Cu saturates the electronics at 40 mg/l
Fe saturates the electronics at 230 mg/l
Mg curvilinear to 40 mg/l becoming non-linear
Na curvilinear to 80 mg/l becoming non-linear

The curvilinear nature of Mg and Na below the levels specified were made acceptable by programming the ICP computer with special calibration curves.

8.1.2 Spectral Interferences. These were described briefly in Sec 3 as applied in this work. It should be stated that a thorough determination of spectral interferences is a lengthy, time-consuming study in itself. Some of the factors influencing the presence or absence and magnitude of interferences are:

1. Wavelength of lines being read.
2. Expected concentrations of the elements involved.
3. Quality and the stability of the system optics. i.e. minimal deterioration with time.

4. Quality and stability of PM tubes and electronics.

5. Purity of chemicals in use.

A thorough study of interferences was conducted prior to the work described in this paper. Many interferences were detected. Those considered relevant were included in the data processing program as listed in Table 4.

8.1.3 Matrix Interferences. Matrix interferences have been observed with respect to the type and quantity of acids used. This has been observed as an enhancement or depression of element emission lines. This effect may be circumvented by careful matrix matching of standards, QC solutions and samples. Careful matches were made for this work.

9. Computations

9.1 Real Time Judgments

9.1.1 Standards, Gains, Offsets. There are virtually no operator computations required by this system with respect to data quantitation. However, the operator is required at numerous points to render a judgment with respect to the validity of numbers generated, and to continue or stop. During the standardization the operator must observe element response to determine if values obtained are normal. In Sec 7.2.2.3, item 4, it was stated that the operator should assess the gains and offsets.

9.1.2 Quality Control Solutions. Two quality control solutions are analyzed alternately every tenth burn (Sec 7.2.2.3). Each of these two solutions contain all elements observed by the spectrometer. The PDP-11 stores expected values and an experience determined bandwidth and performs the relevant comparison immediately upon receipt of the QC data. An immediate indication of any out of control response is displayed on the CRT. When all values are within the tolerance band the computer merely calls for the next sample. When some elements are out of control, operator judgment is involved to determine a course of action. If nearly all elements or NADB reported elements are out of control the cause must be located. Usually this condition is caused by a partially plugged nebulizer. Unreported elements slightly out of control are usually ignored. When the sources of error have been found and corrected the instrument is either rechallenged with the QC standard or restandardized and the 10 samples preceding it are rerun. The original 10 sample analyses are later deleted from the PDP-11 by an editing routine.

9.1.3 Operating Parameters. It is also very important to maintain a daily instrument operating parameters log. A typical log was described previously as Table 7. It is absolutely imperative that the plasma operate in a stable mode with a uniform sample feed rate. Failure to reproduce standards responses and/or QC values usually is caused by a partially or totally plugged nebulizer. The existence of this condition may be verified by observing a decrease in the pump rate or the lack of a fog in the nebulizer spray chamber. A similar effect will be observed if the argon supply pressure or the RF power should change. Experience with the sample pump and the RF power supply have been excellent and both appear to be very stable electronically.

Intermittent failure of QC solutions to fall within the tolerance band may be due to an intermittent failure in a spectrometer circuit or may be due to a broken nebulizer needle. Both are difficult to detect without extensive testing and/or dismantling of equipment. Leaks in the argon supply lines also frequently give rise to similar problems. Leaks in the ground glass joints of the torch-spray chamber have been eliminated by the light use of a good grade stopcock grease (not silicone base).

One intended purpose of the repeated analysis of QC solutions was to detect and correct "within a day" instrument drift. Experience has shown that drift is not a problem when the instrument is standardized twice daily. When drift has been detected it has been attributed to thermal drift and was corrected by reprofiling. It is mandatory to restandardize the instrument after profiling.

Long-term drift is more difficult to detect. A gradual increase in the gains of short wavelength elements over a period of weeks or months is probably due to a degradation of mirror coatings. Washing the mirrors may help in the short-term but usually they will need to be replaced. Gradual degradation of electronic circuits will also cause long-term drift.

The torch and spray chamber occasionally needs to be cleaned. Experience must dictate when as no schedule has been determined nor have any criteria been established. Ultrasonicate in hot detergent for at least 30 minutes, soak in aqua regia overnight and rinse in D.I. water. After reassembling it is mandatory to optimize the torch for maximum flux throughput according to manufacturer's instructions.

Finally, should the plasma be extinguished during an analysis session it is mandatory to end the session and restandardize after reigniting the plasma. Restandardization must be delayed until the reflected power has been at a minimum approximately 10 minutes.

9.2 Post Analysis Judgments

9.2.1 General Information. The PDP-8 of the Jarrell-Ash outputs elemental concentrations in terms of μg/ml to the PDP-11 for storage and data analysis following each sample analysis made during a project analysis period. Project analysis periods may last from several days to a month or more depending on the number of samples to analyze. Virtually all computations are performed by programs available on the PDP-11. The following sections describe the various check samples and solutions analyzed during an analysis period, results of which are then studied to judge the validity of the real sample results. Anomalous data are studied for occurrence patterns and/or related events. Historical data, past experience and additional statistical tests as needed contribute to the decision-making process.

9.2.2 Standard Number One. All determinations of Standard No. 1 made during the analysis period are retrieved by the PDP-11 and the mean and standard deviation computed for each element. The latter when multiplied by 3.3 determines the instrumental detection limit for each element. These are then compared to previous values to evaluate instrument performance.

9.2.3 QC Solutions. The PDP-11 is used to compute the mean, standard deviation and coefficient of variation for each element with the high and low solutions each serving as an individual set. Recoveries are hand computed from this data and all results examined and compared with previous experience. NADB reportable elements usually recover in the range of 97-103%.

9.2.4 Blank Filter Analytical Results. Blank filter strips were analyzed at random during the analysis period. These data are analyzed by the PDP-11 as described in Sec 6.1.1.2 to produce files of mean blank values and discrimination limits for each element. Values obtained should agree with values obtained during acceptance testing, Sec 6.1.1.2.

9.2.5 Sample - Replicate Data. Throughout an analysis period blind replicates are interspersed with the real samples by the EMD QC officer. Following analysis the identities of the blinds are disclosed and sample-replicate data comparisons are made by the PDP-11. Precision is usually 10% or better. Summaries are made available to the EMD QC officer and to DMAD.

9.2.6 QAD Quality Control Strips. Single and/or multi-element spiked 1" x 8" strips submitted by QAD are analyzed at least once a day. Analyses of these are retrieved and results furnished to QAD for further evaluation.

9.2.7 Data Transmittal to DMAD. The PDP-11 performs the following computation for all elements in each sample:

1. Multiplying concentration by 360 to obtain gross μg of the element per filter.
2. Subtract the mean blank value stored for each element from each samples values.
3. Divide the net results by the appropriate air volume which has been stored in another file after transfer from the Univac by magnetic tape.
4. Screen the atmospheric concentration to decide if it is above the discrimination limit which has also been computed by the PDP-11 and stored.

5. Output the results on a magnetic tape as four-letter sample code identifier followed by the alphabetically (by chemical symbol) ordered list of atmospheric values. Values below the discrimination limit are identified by the negative value of L_D for that element. Data are transmitted by magnetic tape to DMAD.

TABLE 1

CONCENTRATIONS OF THE MOST CONCENTRATED WORKING STANDARD

(Note: The Least Concentrated Working Standard Contains no Metals)

Element	ICAP mg/l	Element	ICAP mg/l
Al	50	Nb	2.0
As	5.0	Ni	5.0
Au	5.0	P	20.0
B	10.0	Pb	25
Ba	10.0	Pd	5.0
Be	2.0	Pt	5.0
Bi	10.0	Re	10.0
Ca	40	Rh	5.0
Cd	4.0	Ru	10.0
Ce	5.0	Sb	5.0
Co	5.0	Se	5.0
Cr	4.0	Si	50.0
Cu	20.0	Sm	5.0
Fe	50.0	Sn	5.0
Ge	5.0	Sr	5.0
Hg	5.0	Ta	5.0
In	5.0	Te	5.0
K	20.0	Ti	5.0
La	2.0	Tl	5.0
Li	2.0	V	5.0
Mg	40	W	5.0
Mn	10.0	Y	5.0
Mo	5.0	Zn	20.0
Na	80.0	Zr	5.0

TABLE 2

TYPICAL CALIBRATING SENSITIVITIES

Element	ICAP Output Increment* per 1 μg Metal	Element	ICAP Output Increment* per 1 μg Metal
Al	4,478	Nb	44,287
As	8,280	Ni	10,093
Au	22,081	P	4,780
B	86,465	Pb	7,206
Ba	59,268	Pd	13,525
Be	101,679	Pt	948
Bi	443	Re	291
Ca	116,315	Rh	42,875
Cd	84,402	Ru	5,748
Ce	25,089	Sb	4,984
Co	4,693	Se	2,416
Cr	85,937	Si	12,251
Cu	171,596	Sm	69,869
Fe	36,595	Sn	1,027
Ge	632	Sr	4,602
Hg	18,726	Ta	30,985
In	1,088	Te	8,260
K	1,109	Ti	99,593
La	60,012	Tl	4,518
Li	20,519	V	131,588
Mg	67,270	W	627
Mn	174,062	Y	44,760
Mo	11,893	Zn	2,333
Na	37,693	Zr	30,732

Data Source 79 NASN AM Stds. 3-11-80

*Net values, background corrected. Pump rate 1.85 ml/min,10 sec. exposure, standard conc. as shown in Table 1.

TABLE 3

TYPICAL INSTRUMENTAL DETECTION LIMITS

Element	ICAP mg/l	Element	ICAP mg/l
Al	.010	Nb	.004
As	.005	Ni	.007
Au	.006	P	.06
B	.015	Pb	.011
Ba	.0012	Pd	.09
Be	.0002	Pt	.05
Bi	0.3	Re	.14
Ca	.010	Rh	.58
Cd	.002	Ru	1.2
Ce	.03	Sb	.005
Co	.014	Se	.05
Cr	.007	Si	.06
Cu	.009	Sm	.022
Fe	.014	Sn	.03
Ge	.08	Sr	.004
Hg	.02	Ta	.009
In	.03	Te	.010
K	.07	Ti	.0034
La	.007	Tl	.07
Li	.0008	V	.003
Mg	.006	W	.04
Mn	.002	Y	.001
Mo	.006	Zn	.03
Na	.16	Zr	.006

Data Source 1979 NAMS analyses performed in December 1979.

TABLE 4

SPECTRAL INTERFERENCES - ICP

Affected Element	Factor	Affecting Element	Affected Element	Factor	Affecting Element
Ta	.0166	Co	TL	.0607	Ce
Ta	.0026	Fe	TL	.0229	Zr
Al	.0141	Ta	Zn	.0132	Ta
Al	.0375	V	As	.0088	Al
B	.0181	Zr	As	.1248	Pt
Be	.0020	Nb	As	.0125	V
Be	.0025	V	Bi	.0083	Al
Ce	.2313	V	Vi	.0212	Cr
Mg	.0574	Co	Bi	.0065	Fe
Mg	.0151	Fe	Bi	.0326	La
La	.0028	Fe	Bi	.0155	Mg
La	.0122	V	Bi	.0312	Mn
Pb	.1157	Nb	Bi	.0268	Rh
Pd	.0247	Nb	Bi	.0116	Se
Pd	.1649	Sm	Bi	.0041	Si
Pd	.0125	Ti	Bi	.0125	Sr
Pt	.0600	Cr	Ge	.0161	Al
Pt	.0175	Nb	Ge	.0553	Be
Pt	.1300	Ta	Ge	.0180	Mo
Pt	.0210	V	Ge	.0660	Nb
Si	.0281	Nb	Ge	.0293	Ta
Si	.1300	Ta	P	.0017	Al
Si	.2495	Zr	P	.0265	Cu
Te	.0254	V	P	.0016	Fe

TABLE 4 Cont

Affected Element	Factor	Affecting Element
P	.0032	Mg
P	.0100	Nb
P	.0017	Si
P	.0010	Zn
Re	.0240	Al
Re	.0110	B
Re	.1609	Mn
Re	1.240	Mo
Re	.0556	Pd
Re	.0044	Si
Re	.2146	V
Ru	.0141	Fe
Ru	.0843	Mn
Ru	.0233	Mo
Ru	.0827	Nb
Ru	.2531	Ta
Ru	.0364	Ti
Ru	5.517	V
Ru	.4996	Zr
W	.0021	Al
W	.0039	Mg
W	.0027	Zn

TABLE 5

WORKING STANDARD PREPARATION

Std. No. 1 Zero Standard - No Metals

39.0 ml Ultrex HNO_3
110.4 ml Ultrex HCL
Dilute to 2000 ml with D.I. H_2O
Store in Teflon bottle

Std. No. 2 Eight Metals

Element	Aliquot	Source Section	Substance	Conc. in Final Solu.
Ca	5 ml	6.3.8	Ca Master Std.	40 mg/l
Cd	4 ml	6.3.9	Cd Master Std.	4 mg/l
Co	5 ml	6.3.11	Co Master Std.	5 mg/l
Cu	5 ml	6.3.13	Cu Master Std.	20 mg/l
Mg	5 ml	6.3.21	Mg Master Std.	40 mg/l
Mn	5 ml	6.3.22	Mn Master Std.	10 mg/l
Pb	5 ml	6.3.28	Pb Master Std.	25 mg/l
Zn	5 ml	6.3.47	Zn Master Std.	20 mg/l
	5 ml	6.3.49	1.338 N HCL	

Dilute to 500 ml with Standard No. 1 Store in Teflon bottle

Std. No.3 Fifteen Metals

Element	Aliquot	Source Section	Substance	Conc.in Final Solu.
Al	5 ml	6.3.1	Al Master Std.	50 mg/l
Ba	5 ml	6.3.5	Ba Master Std.	10 mg/l
Be	2 ml	6.3.6	Be Master Std.	2 mg/l
Fe	5 ml	6.3.14	Fe Master Std.	50 mg/l
Li	2 ml	6.3.20	Li Master Std.	2 mg/l
Mo	5 ml	6.3.23	Mo Master Std.	5 mg/l
Na	4 ml	6.3.24	Na Master Std.	80 mg/l

TABLE 5 (Cont.)

WORKING STANDARD PREPARATION

Std. No 3 (cont.)

Element	Aliquot	Source Section	Source Substance	Conc.in Final Solu.
Ni	5 ml	6.3.26	Ni Master Std.	5 mg/l
Sb	5 ml	6.3.34	Sb Master Std.	5 mg/l
Sn	5 ml	6.3.38	Sn Master Std.	5 mg/l
Sr	5 ml	6.3.39	Sr Master Std.	5 mg/l
Ti	5 ml	6.3.42	Ti Master Std.	5 mg/l
Tl	5 ml	6.3.43	Tl Master Std.	5 mg/l
V	5 ml	6.3.44	V Master Std.	5 mg/l
Zr	5 ml	6.3.48	Zr Master Std.	5 mg/l

Dilute to 500 ml with Standard No. 1 Store in Teflon bottle

Std.No. 4 Eight Metals

Element	Aliquot	Source Section	Source Substance	Conc.in Final Solu.
As	5 ml	6.3.2	As Master Std.	5 ml/l
B	5 ml	6.3.4	B Master Std.	10 ml/l
Cr	4 ml	6.3.12	Cr Master Std.	4 mg/l
Ge	5 ml	6.3.15	Ge Master Std.	5 mg/l
P	5 ml	6.3.27	P Master Std.	20 mg/l
Se	5 ml	6.3.35	Se Master Std.	5 mg/l
Si	5 ml	6.3.36	Si Master Std.	50 mg/l
Te	5 ml	6.3.41	Te Master Std.	5 mg/l

To 500 ml with Standard No. 1 Store in Teflon bottle

TABLE 5 (Cont.)

WORKING STANDARD PREPARATION

Std. No. 5 Seventeen Metals

Element	Aliquot	Source Section	Source Substance	Conc. in Final Solu.
Au	5 ml	6.3.3	Au Master Std.	5 mg/l
Bi	5 ml	6.3.7	Bi Master Std.	10 mg/l
Ce	5 ml	6.3.10	Ce Master Std.	5 mg/l
Hg	5 ml	6.3.16	Hg Master Std.	5 mg/l
In	5 ml	6.3.17	In Master Std.	5 mg/l
K	5 ml	6.3.18	K Master Std.	20 mg/l
La	2 ml	6.3.19	La Master Std.	2 mg/l
Nb	2 ml	6.3.25	Nb Master Std.	2 mg/l
Pb	5 ml	6.3.29	Pb Master Std.	5 mg/l
Pt	5 ml	6.3.30	Pt Master Std.	5 mg/l
Re	5 ml	6.3.31	Re Master Std.	10 mg/l
Rh	5 ml	6.3.32	Rh Master Std.	5 mg/l
Ru	5 ml	6.3.33	Ru Master Std.	10 mg/l
Sm	5 ml	6.3.37	Sm Master Std.	5 mg/l
Ta	5 ml	6.3.40	Ta Master Std.	5 mg/l
W	5 ml	6.3.45	W Master Std.	5 mg/l
Y	5 ml	6.3.46	Y Master Std.	5 mg/l
	10 ml		1.338 N Hcl	

To 500 ml with Standard No. 1 Store in Teflon bottle

TABLE 6

HI QC SOLUTION - JACO - PLSN ROUTINE

Prepare from Master Calibration Standards, Section 6.3

Element	Conc	Ml Stock
Al	40	8
As	4	8
Au	4	8
B	8	8
Ba	8	8
Be	1.5	3
Bi	8	8
Ca	32	8
Cd	3	6
Ce	4	8
Co	4	8
Cr	3	6
Cu	16	8
Fe	40	8
Ge	4	8
Hg	4	8
In	4	8
K	16	8
La	1.5	3
Li	1.5	3
Mg	32	8
Mn	8	8
Mo	4	8
Na	60	6
Nb	1.5	3
Ni	4	8
P	16	8
Pb	20	8
Pd	4	8
Pt	4	8
Re	8	8
Rh	4	8
Ru	8	8
Sb	4	8
Se	4	8
Si	40	8
Sm	4	8
Sn	4	8
Sr	4	8
Ta	4	8
Te	4	8
Ti	4	8
Tl	4	8
V	4	8
W	4	8
Y	4	8
Zn	16	8
Zr	4	8
1.338N Hcl		24

To 1 liter with standard No. 1

TABLE 7

TYPICAL INSTRUMENT OPERATING PARAMETERS RECORD

JARRELL-ASH PLASMA ATOMCOMP OERPATING PARAMETERS

DATE: 3/11/80 PROJECT: N79 OPERATOR: MO.L

OBJECTIVE: 1979 NASN Samples

PROFILE SETTING: 594.4/587.7 TIME PLASMA ON: 0735 TIME OF STDS: 0833

OBSERVATION ZONE: 16mm SETTINGS-AUTO: 5.96 MATCHBOX: 10.75

TIME	SAMPLE UPTAKE				AFGON		POWER		COMMENTS
	ML.	MIN.	SEC.	RATE	COOL. LPM.	NEBUL. PSI.	FWD. KW.	REF. W.	
0830	2	1	4.6	1.86	18	16	1.1	13	Before stds
0919	2	1	4.8	1.85	18	16	1.1	13	After 21 burns
0947	2	1	4.6	1.86	18	16	1.1	13	After 41 burns
1013	2	1	4.2	1.87	18	16	1.1	13	After 61 burns
1046	2	1	4.6	1.86	18	16	1.1	13	After 81 burns
1112	2	1	4.8	1.85	18	16	1.1	13	After 101 burns
1141	2	1	4.4	1.86	18	16	1.1	13	After 121 burns
1226	2	1	5.2	1.84	18	16	1.1	13	After 152 burns
	End session —								
1259	2	1	4.4	1.86	18	16	1.1	13	Before stds
1346	2	1	4.4	1.86	18	16	1.1	13	After 21 burns
1413	2	1	4.6	1.86	18	16	1.1	13	After 41 burns
1439	2	1	4.2	1.87	18	16	1.1	13	After 61 burns
1505	2	1	4.8	1.85	18	16	1.1	13	After 81 burns
1530	2	1	4.4	1.86	18	16	1.1	13	After 101 burns
1556	2	1	4.2	1.87	18	16	1.1	13	After 121 burns
1632	2	1	4.6	1.86	18	16	1.1	13	After 150 burns
	End session								

302 burns today

Profile	0826	1254	
	649.1	645.2	
	540.0	531.0	(30)
[illegible]	[illegible]	[illegible]	[illegible]
36.0	[illegible]	[illegible]	36.2

10. Bibliography

1. Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method). Code of Federal Regulations, Title 40, Part 50, Appendix B, pp. 12-16, (July 1, 1975).

2. Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air. Federal Register, Vol. 42, No. 240, Appendix G., pp. 63080-63085, (Dec. 14, 1977).

1.4.2 Quality Control Procedures

Quality control procedures to be applied to the analysis of metals on hi-vol filters are described in some detail below. These activities are an expansion on or in addition to the quality control procedures presented as part of the analytical method in Section 1.4.1 of this Appendix. The frequency, control limits and corrective action for each item are summarized in Table 1-3.

A. Calibration and Standardization

Procedures for the calibration and standardization of the instrument are discussed on page 40 of 60 of Section 1.4.1 of this Appendix. These include the analysis of five working standards in duplicate and utilization of the average ratio of the two burns for the calibration curve. Calibration and preliminary checks of known QC samples are required for each session of running (approximately 3 to 3-1/2 hours).

B. Calibration Check

A check calibration standard is run after every 20 samples analyzed. This is generally the zero standard. In addition, known QC samples, designated HIQC and LOQC, which contain all elements seen by the instrument, are run after every 10 samples analyzed. These QC samples are used to monitor instrument drift and to facilitate early detection of instrumental problems. Performance within the control limits for these QC samples is checked automatically by the instrument computer prior to analysis of the next environmental sample. Observed recovery for the QC samples is usually in the range of 97 to 103 percent.

C. Method Blanks

Prior to the initiation of this study, a series of thirty (30) blank hi-vol filters will be taken through the entire analytical procedure to determine mean background levels of each metal. These values will be used to correct sample values for contribution from the filter medium. In addition, blank filters will be randomly interspersed with the field samples at a frequency of 1 in 20 samples to monitor detected background levels in the filters. Blank values will be evaluated in terms of the mean and discrimination limit determined in the preliminary filter study.

Method blanks consisting only of the reagents use for filter extractions are to be tested for detectable levels of the metals of interest prior to the start of the program. Additional reagents blanks may be processed with each sample batch to detect contamination entering samples through the analytical process. It is highly recommended, though not required, that reagent blanks be run with each batch of samples analyzed. One (1) reagent blank for each group of fifty (5) samples should be sufficient to detect analytical problems.

TABLE 1-3. INTERNAL QC REQUIREMENTS - METALS IN AIR

Operation check	Frequency	Control limits	Corrective action planned
Calibration and standardization	For each analysis session (3-3 1/2 hours)	Not applicable	Not applicable
Calibration checks	Zero standard after every 20 samples LOQC or HIQC after every 10 samples	No significant drift observed Specified in computer control program	Check analytical procedure Analyze second reference sample Invalidate results and recalibrate
Method blank (blank hi-vol filter	Thirty (30) filters prior to start of analysis	Establish mean levels and discrimination limit for each metal	Not applicable
	One blank for every 20 samples	No significant concentrations found; levels meet criteria established in preliminary study	Check analytical procedure Analyze reference sample Analyze reagent blank Invalidate results
Method blank (reagent water)	Preliminary check plus optional analysis of one (1) reagent blank per 50 samples	No significant concentrations found	Check analytical procedure Analyze reference sample Invalidate results
Replicate analysis	One (1) of every 20 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

D. Replicate Analyses

Random samples will be chosen for replicate analysis and interspersed with environmental samples by the laboratory QC officer. One (1) sample in 20 samples is subjected to replication. A replicate (split) is a second aliquot of a sample that is carried through the entire analytical procedure. The results of duplicate analyses will be used to evaluate intralaboratory precision of the environmental measurements and to establish validity of the data.

1.5 DIOXINS (Tetrachlorodibenzo-p-dioxins)

1.5.1 Analytical Procedures

Air samples are collected by drawing air through polyurethane foam plugs; dioxins present inthe air are assumed to be trapped or solved by the foam plug.

Foam plug samples are soxhlet-extracted with benzene for 16 hours. The extract is concentrated, subjected to various washing and liquid chromatographic procedures to remove organic interferences and the dioxins (TCDDs) present in the extract determined by gas chromatography-mass spectrometry. 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is used as a standard for quantifying samples and $^{37}Cl_4$-2,3,7,8-TCDD is used as an internal standard.

This section contains the extraction and washing procedures specific to foam plugs; the extract produced is then handled as directed in Section 7.6 of this appendix. Quality Control procedures for foam plug samples are given in Section 1.5.2.

A. Sample Handling and Preservation

TCDD is toxic and can pose grave health hazards if handled improperly. Techniques used for handling radioactive and infectious material are applicable and only qualified individuals trained in laboratory procedures and familiar with the hazards of TCDD should handle this substance. Females of childbearing age should not work with this material.

Polyurethane foam plugs for dioxin analysis are received by the laboratory according to chain-of-custody procedures and internal chain-of-custody must be maintained. As received, the foam plug samples should be enclosed in the glass sampling module and wrapped in hexane-rinsed aluminum foil. They should be maintained in this condition until time for analysis. No chemical preservation is used and storage should be at ambient temperature.

B. Reagents

- Potassium hydroxide, anhydrous sodium sulfate, and sulfuric acid, ACS Reagent Grade,
- Methanol, hexane, methylene chloride and benzene, "Distilled in Glass" quality,
- Petroleum ether (low boiling), Omnisone Quality from Matheson, Coleman, and Bell, or equivalent,
- WOELM basic alumina, Activity Grade 1,
- Prepurified nitrogen gas,
- Double-distilled water

- Dioxin standards can be obtained from the sources listed below:

$^{37}Cl_4$-2,3,7,8-TCDD-KOR Isotopes, Cambridge, Mass.
1,2,3,4-TCDD-Analabs, Inc., North Haven, Connecticut
2,3,7,8-TCDD-Dow Chemical Co., Midland, Michigan

1,3,6,8 1,3,7,9 1,4,6,9 1,3,7,8 1,2,6,8 1,2,7,9 1,2,6,9 1,2,7,8 1,2,6,7 1,2,8,9	H. R. Buser Swiss Federal Research Station Ch-820 Wadenswil, Switzerland

C. Sample Extraction/Cleanup Procedures

1. Remove foam plug from shipping container and place in clean soxhlet extractor.

2. Spike the foam with the internal standard (25 µl of a benzene solution containing 1ng $^{37}Cl_4$-2,3,7,8-TCDD per µl is added directly to the foam).

3. Extract the foam plug for 16 hours using benzene as the extraction solvent.

4. Concentrate the extract to about 0.5 mL in a stream of prepurified nitrogen while heating the sample in a 55° water bath.

5. Add 40 ml of hexane to the extract and quantitatively transfer the solution to a clean 125 mL flint glass bottle.

6. Extract the organic solution with 50 mL of 20% (w/v) potassium hydroxide by shaking for 10 minutes. Allow for complete separation and remove aqueous base (bottom) layer to base waste bottle.

7. Extract the organic solution with 50 mL of doubly distilled water by shaking the sample for 2 minutes. Allow time for complete layer separation and discard the aqueous (bottom) layer.

8. Extract the organic solution with 50 mL of concentrated sulfuric acid (cautiously adding sulfuric acid) by shaking the sample for 15 minutes. Allow for complete layer separation and discard acid (bottom) layer into acid waste bottle.

9. Repeat Step 8 until acid layer is nearly transparent.

10. Extract the organic solution with 50 mL of doubly distilled water by shaking for 2 minutes. Allow for complete separation and remove aqueous (bottom) layer.

11. Dry the organic layer over sodium sulfate and then quantitatively transfer a portion of the organic layer to a clean test tube and reduce the volume to incipient dryness using a stream of prepurified nitrogen and while maintaining the test tube in a 55° water bath.

The dried extract should now be further cleaned up using the procedure given in Section 7.6 of this Appendix. This section also contains GC/MS analysis specifications, analytical criteria for positive TCDD results and reference material.

D. Reporting of Analytical Results

Analytical results must satisfy specific analytical criteria to be considered positive results. The criteria used by the EPA Health Effects Research Laboratory (HERL)/RTP for TCDD are given in Section 7.6 of this Appendix. Only analytical results meeting these or comparable criteria should be reported. All positive results on collected samples will be confirmed by the EPA referee laboratory, HERL/RTP.

The analytical results reported for each sample should include: sample identification, percent recovery for TCDD, minimum limits of detection for TCDDs (ng/plug), TCDDs detected (ng/plug), and comments pertaining to each analysis as necessary.

1.5.2 Quality Control Procedures

Quality control procedures to be utilized in the analysis of TCDD are described below in some detail. In addition, the QC activities and the type, frequency, control limits and corrective action for each are summarized in Table 1-4.

A. Calibration and Standardization

A calibration curve is prepared by analyzing a series of standard solutions containing varying concentrations of 2,3,7,8-TCDD; each standard solution contains the same concentration of $^{37}Cl_4$-2,3,7,8-TCDD. The ratio of the areas of the peaks which are indicative of 2,3,7,8-TCDD and $^{37}Cl_4$-2,3,7,8-TCDD is plotted as a function of the concentration of 2,3,7,8-TCDD. Use of the internal standard technique automatically corrects the results for any losses of TCDD incurred during sample processing.

B. Calibration Check Standards/Standard Validation

Primary quantification standards containing both 2,3,7,8-TCDD and $^{37}Cl_4$-2,3,7,8-TCDD are prepared by EPA, HERL/RTP and submitted to the analytical laboratory by the Prime Contractor for use in validating the laboratory's TCDD standards.

C. Control Samples/Method Validation

Prior to actual analysis, the methodology which has been developed is tested and optimized by analyzing a series of control samples - blank foam plugs to which known quantities of TCDD have been added. These samples are spiked by personnel other than those involved in the actual analysis, and the analysts do not know the level of TCDD added to the sample until after the results of their analysis have been reported. Generally, for samples such as those analyzed in this project, the method is deemed acceptable if 70-100 percent of the added TCDD is recovered and detected in the analysis. If this is not the case, then modifications are made to the method to further optimize the performance, and additional spiked samples are analyzed using the revised procedures. This is repeated until a satisfactory level of performance is obtained for the spiked samples.

D. Laboratory Control Standards (LCS)

Blank foam plugs spiked with TCDD are used as laboratory control standards (LCS) to identify any systematic method or operator errors. If the recovery for the LCS is not within the acceptance limits identified during the method validation, then an entire new series of LCS analyses is repeated, and the methodology is thoroughly checked to determine the source of error. Selected Love Canal samples analyzed during any period when unacceptable QC data are obtained are also reanalyzed to ensure that these were not affected by any temporary aberrations in the methods or procedures.

TABLE 1-4. INTERNAL QC REQUIREMENTS--DIOXINS IN AIR

Operation check	Frequency	Control limits	Corrective action planned
Calibration of instrument	Daily before analysis of samples	Not applicable	Not applicable
Internal standard	Added to every sample and standard	To be determined	Report percent recovery Check analytical procedure
Calibration check	One per analysis batch[a]	To be determined	Check analytical procedure Analyze second reference standard Invalidate results and generate fresh standard curve
Method Validation	Before use of new sample cleanup/ analysis procedures	To be determined	Modify cleanup or analysis procedure
Laboratory control standard (LCS)	One per analysis batch[a]	As determined in Method validation	Check analytical procedure Analyze second reference sample Invalidate results
Method blank	One per analysis batch[a]	No significant concentrations found	Correct for blank Check analytical procedure
Analytical criteria	Each positive TCDD result	As in Section 7.6, or equivalent	Report TCDD not detected

[a] Analysis batch = group of samples processes as a set, usually containing 15 samples or less.

E. Method Blanks

One method blank (blank foam plug) shall be carried through the sample preparation and analysis procedures to ensure that sample results can be corrected for compounds contributed by the reagents and chemicals used in the procedures.

F. Analytical Criteria/Confirmation of Positive Results

All positive TCDD results are tested by the criteria given in Section 7.6 or equivalent criteria, before reporting. The extracts of samples in which native TCDDs have been found are sent to the EPA referee laboratory, HERL/RTP for confirmatory analyses.

2.0 WATER ANALYSIS

2.1 OVERVIEW

This section outlines procedures for the analysis of sump, ground, drinking, sewer and surface waters for the following pollutant classes.

- 2.2 Volatile Organics
- 2.3 Semivolatile Organics
- 2.4 Pesticides
- 2.5 Metals
- 2.6 Selected Anions (Fluoride and Nitrate)
- 2.7 Total Organic Carbon (TOC)
- 2.8 Total Organic Halogens (TOX)
- 2.9 Dioxins
- 2.10 Radioactivity

Table 2-1 lists the specific parameters of interest for both organic and inorganic analyses.

Any quality control procedures specified by the analytical methods are to be followed; the following quality control procedures are a part of all analyses.

1. Method Blanks
2. Replicate Analyses
3. Surrogates or Spikes
4. Laboratory Control Standards

Specific quality control requirements are detailed in each section.

Sample preservation, in addition to storage at 4°C, will be performed in the field as part of several analyses. These sample preservation procedures are stated with the analytical procedures for each parameter.

TABLE 2-1. CHEMICALS TO BE MONITORED IN LOVE CANAL

Compound, Element, or Ion	CAS registry number
Volatiles	
methylene chloride	75-09-2
chloromethane	74-87-3
1,1-dichloroethene	75-35-4
bromomethane	74-83-9
1,1-dichloroethane	75-34-3
vinyl chloride	75-01-4
cis-1,2-dichloroethene	156-59-2
chloroethane	75-00-3
trans -1,2-dichloroethene	156-60-5
trichlorofluoromethane	75-69-4
chloroform	67-66-3
1,2-dichloroethane	107-06-2
1,1,1-trichloroethane	71-55-6
carbon tetrachloride	56-23-5
bromochloromethane	74-97-5
bromodichloromethane	75-27-4
2,3-dichloropropene[1]	78-88-6
1,2-dichloropropane	78-87-5
trichloroethene	79-01-6
trans -1,3-dichloropropene	10061-02-6
benzene	71-43-2
acrolein[1]	107-02-8
acrylonitrile[1]	107-13-1
dibromochloromethane	124-48-1
1,1,2-trichloroethane	79-00-5
bromoform	75-25-2
1,1,2,2-tetrachloroethane	79-34-5
benzyl chloride	100-44-7
o-xylene	95-47-6
m-xylene	108-38-3
p-xylene	106-42-3
tetrachloroethene	127-18-4
toluene	108-88-3
2-chlorotoluene	95-49-8
3-chlorotoluene	108-41-8
4-chlorotoluene	106-43-4
chlorobenzene	108-90-7
ethyl benzene	100-41-4
1,2-dibromoethane	106-93-4

(continued)

TABLE 2-1 (continued)

Compound, Element, or Ion	CAS registry number
Semi-volatiles	
hexachloroethane	67-72-1
1,4-dichlorobenzene	106-46-7
1,3-dichlorobenzene	541-73-1
1,2-dichlorobenzene	95-50-1
bis(2-chloroethyl)ether	111-44-4
bis(2-chloroisopropyl)ether	39638-32-9
N-nitrosodi-n-propylamine	621-64-7
hexachlorobutadiene	87-68-3
1,2,3-trichlorobenzene	87-61-5
N-nitrosodimethylamine[2]	62-75-9
1,2,4-trichlorobenzene	120-82-1
1,3,5-trichlorobenzene	108-70-3
nitrobenzene	98-95-3
naphthalene	91-20-3
isophorone	78-59-1
bis(2-chloroethoxy)methane	111-91-1
hexachlorocyclopentadiene[3]	77-47-4
2-chloronaphthalene	91-58-7
acenaphthylene	208-96-8
acenaphthene	83-32-9
dimethylphthalate	131-11-3
2,6-dinitrotoluene	606-20-2
fluorene	86-73-7
1,2-diphenylhydrazine[4]	122-66-7
4-chlorophenylphenyl ether	7005-72-3
2,4-dinitrotoluene	121-14-2
2,4-dichlorotoluene	95-73-8
diethylphthalate	84-66-2
N-nitrosodiphenylamine[5]	86-30-6
hexachlorobenzene	118-74-1
4-bromophenylphenylether	101-55-3
phenanthrene	85-01-8
anthracene	120-12-7
di-n-butyl phthalate	84-74-2
fluoranthene	206-44-0
pyrene	129-00-0
benzidine[6]	92-87-5
butylbenzylphthalate	85-68-7
di(2-ethylhexyl)phthalate	117-81-7
chrysene	218-01-9
di-n-octylphthalate	117-84-0
benzo(a)anthracene	56-55-3
benzo(k)fluoranthene	207-08-9
benzo(b)fluoranthene	205-99-2
benzo(a)pyrene	50-32-8

(continued)

TABLE 2-1 (continued)

Compound, Element or Ion	CAS registry number
3,3-dichlorobenzidine	91-94-1
indeno(1,2,3-dc)pyrene	193-39-5
dibenzo(a,h)anthracene	53-70-3
benzo(g,h,i)perylene	191-24-2
pentachloronitrobenzene	82-68-8
2,4,6-trichloroaniline	634-93-5
4-chlorobenzotrifluoride (trifluoro-p-chlorotoluene)	98-56-6
1,2,3,4-tetrachlorobenzene	634-66-2
1,2,4,5-tetrachlorobenzene	95-94-3
2,3,7,8-tetrachlorodibenzo-p-dioxin (selected samples only)	1746-01-6
tetrachlorotoluenes (18 position isomers - ring and methyl substitution)	
2-chlorophenol	96-57-8
3-chlorophenol	108-43-0
4-chlorophenol	106-48-9
2-nitrophenol	88-75-5
phenol	108-95-2
2,4-dimethylphenol	105-67-9
2,4-dichlorophenol	120-83-2
2,3,6-trichlorophenol	933-75-5
2,4,6-trichlorophenol	88-06-2
4-chloro-3-methylphenol	59-50-7
2,4-dinitrophenol	51-28-5
2-methyl-4,6-dinitrophenol	534-52-1
pentachlorophenol	87-86-5
4-nitrophenol	100-02-7
Pesticides	
alpha-BHC[7]	319-84-6
beta-BHC	319-85-7
gamma-BHC[7]	58-89-9
delta-BHC	319-86-8
heptachlor	76-44-8
aldrin	309-00-2
mirex	2385-85-5
endosulfan I[7]	33213-65-9
heptachlor epoxide	1024-57-3
DDE	72-55-9
endrin[7]	72-20-8
endosulfan II[7]	959-98-8
dieldrin	60-57-1
endosulfan sulfate	1031-07-8
DDD	72-54-8

(continued)

TABLE 2-1 (continued)

Compound, Element or Ion	CAS registry number
chlordane	57-74-9
DDT	50-29-3
toxaphene	8001-35-2
aroclor 1221	11104-28-2
aroclor 1254	11097-69-1
aroclor 1016	12674-11-2
aroclor 1232	11141-16-5
aroclor 1242	53469-21-9
aroclor 1248	12672-29-6
aroclor 1260	11096-82-5
Inorganics	
antimony	
arsenic	
barium	
beryllium	
cadmium	
chromium	
copper	
lead	
mercury	
nickel	
selenium	
silver	
thallium	
zinc	
fluoride } water samples only	
nitrate } water samples only	

(continued)

TABLE 2-1 (continued)

FOOTNOTES

1. These compounds may be observed to about 1 milligram per liter with Method 624. If detected the quantitative analysis must be accomplished by purging a second aliquot of the sample at 85°C as described in Method 603.

2. This compound is not resolved from the solvent with the standard columns required for Method 625. It may be resolved with a 30 meter fused silica SE 54 capillary column.

3. This compound decomposes in the injection port at the temperature required for Method 625. A second injection at a low injection port temperature is required to observe this compound when using the standard Method 625 columns. However, this compound is sufficiently stable for analysis with the 30 meter fused silica SE 54 capillary column.

4. This compound decomposes in the GC injection port to azobenzene, and cannot be distinguished from it by 70 ev mass spectrometry. If observed it must be reported as 1,2-diphenylhydrazine or azobenzene.

5. This compound decomposes in the GC injection port to diphenylamine, and cannot be distinguished from it by 70 ev mass spectrometry. If observed it must be reported as N-nitrosodiphenylamine or diphenylamine.

6. This compound is decomposed during the solvent concentration and drying steps of Method 625. It may be observed, but the concentration measurement cannot be considered reliable. It must be confirmed using an alternative method such as Method 605 (Federal Register, December 3, 1979).

7. These compounds are sensitive to the pH=12 extraction conditions of Method 625 and are not observed under normal conditions. These compounds must be measured using Method 608 with confirmation by GC/MS using the Method 608 extracts.

2.2 VOLATILE ORGANICS

2.2.1 Analytical Procedure

Volatile organic compounds, or purgeables, are measured using the methods and techniques described in the Federal Register of 3 December 1979 under Method 624. A copy of this procedure, in its entirety, is included in Section 7.4 of the reference material. Characteristic ions for compounds of interest to this study but not included in Method 624 are given in Table 2-2.

TABLE 2-2. CHARACTERISTIC IONS FOR COMPOUNDS NOT INCLUDED IN METHOD 624

Compound	EI ions			Primary ions
benzyl chloride	91	126		91
o-xylene	91	106	105	106
m-xylene	91	106	105	106
p-xylene	91	106	105	106
2-chlorotoluene	91	126		91
3-chlorotoluene	91	126		91
4-chlorotoluene	91	126		91
1,2-dibromoethane	27	107	109	107

As specified in Section 1.6 of Method 624, acrolein and acrylonitrile cannot be accurately quantitated by this procedure. If these compounds are observed in the samples, a second aliquot of the same sample (held in reserve) should be analyzed using Method 603, Federal Register, 3 December 1979. A copy of Method 603 appears in Section 7.1 of the reference material.

Preservation for each type of water sample for volatiles analysis should have been performed in the field as follows:

Sample type	Preservation	Amount
Drinking water	2% $Na_2S_2O_3$	10 mg/vial = 0.5 ml
Groundwater	None	Not applicable
Sump, sewer, drain and surface waters	None	Not applicable

All samples are to be maintained at 4°C.

2.2.2 Quality Control Procedures

Quality control procedures to be followed in this analysis are described below. Included are the requirements for instrument calibration and the frequency and type of internal QC samples to be run. Each activity is described in some detail with references to standard methods made where appropriate. In addition, a summary of the frequency, control limits, and corrective action for each is given in Table 2-3. Procedures required for each batch of Method 603 analyses are as designated by footnotes to Table 2-3.

A. Tuning of Mass Spectrometer

Daily measurements of the GC/MS standard reference compound decafluorotriphenylphosphine (DFTPP) and/or 4-bromofluorobenzene (BFB) must be made. The procedures and criteria to be met for DFTPP are as set forth in Method 625. The procedure for BFB is injection of 50 nanograms of 4-bromofluorobenzene into the gas chromatograph with the following acceptance criteria applying:

Mass	Ion Abundance Criteria
50	15-40% of the base peak
75	30-60% of the base peak
95	base peak, 100% relative abundance
96	5-9% of the base peak
173	less than 1% of the base peak
174	greater than 50% of the base peak
175	5-9% of mass 174
176	greater than 50% of the base peak
176	greater than 94% but less than 100% of 174
177	5-9% of mass 176

The specified criteria must be met prior to the analysis of samples of each analysis day. This data must be recorded and provided to the Prime Contractor.

B. Calibration of GC/MS System

The GC/MS system must be initially calibrated to determine response factors using standards described in Section 6 of Method 624. After the system has been calibrated, the calibration for organic compounds must be verified at least once each day of running (8 hours) by the use of standards containing, if applicable, the internal standard(s). If the deviation is greater than 20 percent, the system must be recalibrated. Information regarding the verification of calibration should be recorded and provided to the Prime Contractor.

C. Purging Efficiency

The purging efficiency of the system must be determined each day for analysis of acrolein and acrylonitrile by Method 603. A mixed standard of these two compounds must be analyzed each day prior to analysis of these compounds by Method 603. Control limits for recovery are as follows:

TABLE 2-3. INTERNAL QC REQUIREMENTS — VOLATILE ORGANICS IN WATER

Operation check	Frequency	Control limits	Corrective action planned
Tuning of mass spectrometer[a]	Daily before analysis of samples	Table 3 of Method 624[b] or as specified in text	Retune spectrometer
Check purging efficiency of acrolein/acrylonitrile[c]	Daily before analysis of samples	Acrolein 80-90% Acrylonitrile 93-103%	Check analytical procedure
Method blank[a] (reagent water)	Daily-before analysis batch[d]/ analysis day	No significance concentrations found	Check analytical procedure Correct for blank
Calibration check of GC/MS system	Once per 8 hours of analysis time	Deviation less than ±20 percent	Recalibrate system
Internal standards	Optional addition to each sample	Section 6.4 of Method 624[b]	Check analytical procedure Analyze reference sample Invalidate results
Surrogate compounds	Addition to each sample	As specified in text	Check analytical procedure Analyze reference sample Invalidate results
Laboratory control standard (LCS)[a]	One per analysis batch[d]/ analysis day	As specified in text	Check analytical procedure Analyze second reference sample Invalidate results
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

[a] Applicable to analysis by Method 603 as well as Method 624.

[b] A copy of Method 624 appears in Section 7.4 of this Appendix.

[c] Applicable only to Method 603.

[d] Analysis batch = group of samples processed as a set, usually containing 15 samples or less.

Compound	Control limit
Acrolein	80 - 90%
Acrylonitrile	93 - 103%

D. Internal Standards

For the analysis of volatile organic compounds in water by Method 624, external standardization is an acceptable approach to quantification. If the use of internal standards is preferred, however, the following compounds will be acceptable to this program:

1,4-difluorobenzene

pentafluorobenzene

2-bromo-1-chloropropane

The 1,4-difluorobenzene and pentafluorobenzene compounds will be provided by the U.S. EPA, Health Effects Research Laboratory, Cincinnati, Ohio. The use of 2-bromo-1-chloropropane as an internal standard, while acceptable, is cautioned owing to its possible presence in Love Canal samples. Procedures for the use of internal standards are those given in Section 5.6 and 6.4 of Method 624.

E. Surrogate Compounds

Surrogate organic compounds will be added at a known concentration of 5-25 micrograms per liter to every environmental sample. Surrogate compounds for volatiles in water and acceptable control limits expressed as percentage of true value are as follows:

Compound	Control limit
Fluorobenzene	81 - 107%
p-Bromofluorobenzene	88 - 118%

F. Laboratory Control Standards

Laboratory control standards (LCS) will be employed to identify systematic method and operator errors. The LCS is a mixture of a number of compounds of known concentration in a reference material or spiked into reagent water. They are prepared from EMSL-Cincinnati QC concentrates or standards supplied by the individual laboratory. A minimum of the compounds to be used to make up the LCS for volatile organic analyses is outlined below. For Method 624, there must be one LCS processed through the entire analytical method for each set of samples processed in a group on the same day. Normally, this will be one LCS for every 5 to 15 samples. A control chart should be maintained for each of the compounds with the control limits below (calculated as percent of true value) demonstrating acceptable performance.

The following standard mixtures are recommended for use as a laboratory control standard for purgeables (Method 624 or Method 603). The LCS should contain these compounds in the range of 5-25 μg/l:

	Compound	Control limits
Method 624:	Benzene	79 - 107%
	Chloroform	90 - 100%
	Bromoform	76 - 107%
	sym-Tetrachloroethane	67 - 110%
	p-Bromofluorobenzene	88 - 118%
	Carbon tetrachloride	85 - 102%
	Fluorobenzene	81 - 107%
	Trichloroethylene	93 - 105%
	Tetrachloroethylene	93 - 120%
	Chlorobenzene	69 - 107%
Method 603:	Acrolein	To be determined
	Acrylonitrile	To be determined

G. Method Blanks

One method blank (reagent water) must be processed through the entire analytical procedure for every set of samples processed in a group at the same time on the same day. At least one method blank must be run per work shift. The method blank must not show any signals that correspond to compounds on the Love Canal or priority pollutants lists. If common laboratory contaminants are found in the method blanks, reported values for the same compounds in the environmental samples must be reduced by the amount found in the blank.

H. Replicate Analyses

Intralaboratory precision of the environmental measurements will be evaluated by the measurement of one duplicate (split) of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These results must be reported as part of the data base on the Love Canal Study.

2.3 SEMIVOLATILE ORGANICS

2.3.1 Analytical Procedures

The procedures to be followed for analysis of semivolatiles in water are based on Method 625 for Base/Neutrals, Acids and Pesticides as it appeared in the Federal Register of 3 December 1979. A full copy of the procedure is included in Section 7.5 of the reference material. A number of compounds on the Love Canal Monitoring List are not included in the standard Method 625; Table 2-4 gives characteristic ions for these compounds to facilitate their identification.

TABLE 2-4. CHARACTERISTIC IONS FOR COMPOUNDS NOT INCLUDED IN METHOD 625

	EI ions			Primary ions
1,2,3-trichlorobenzene	180	182	184	180
1,3,5-trichlorobenzene	180	182	184	180
2,4-dichlorotoluene	125	160	162	160
pentachloronitrobenzene	249	293	295	293
2,4,6-trichloroaniline	195	197	199	195
4-chlorobenzotrifluoride				
1,2,3,4-tetrachlorobenzene	214	216	218	214
1,2,4,5-tetrachlorobenzene	214	216	218	214
tetrachlorotoluenes (18 isomers)				
3-chlorophenol	65	128	130	128
4-chlorophenol	65	128	130	128
2,3,6-trichlorophenol	196	198	200	196

The semivolatiles in water will be measured using four extraction and analysis schemes designated Methods A,B,C, and D. These methods which include the standard Method 625 and variations on that procedure are described in some detail.

Preservation of samples for semivolatiles analysis as should have been performed in the field for each type of water is as follows:

Sample type	Preservative(s)	Amount
Drinking water	3.5% $Na_2S_2O_3$	35 mg/l = 1 ml
Groundwater	None	Not applicable
Sump, sewer, drain and surface waters	None	Not applicable

All samples are to be maintained at 4°C.

A. Method A

The procedures described in Method 625, Base Neutrals, Acids and Pesticides (Federal Register, Vol. 44, No. 233, 3 December 1979) are to be followed for this analysis with the additions, deletions and comments enumerated below. Method 625 is reproduced in Section 7.5 of this Appendix.

1. Analysis of the individual extracts must be by packed column GC/MS.

2. Hexachlorocyclopentadiene decomposes in the injection port at the temperature required by Method 625. A second injection at a lower injection port temperature is required for quantitation should it be qualitatively identified in a sample by Method 625.

3. Benzidine decomposes during the concentration and drying steps of Method 625. It may be observed but the concentration measurements cannot be considered reliable and a second analysis must be performed if it is detected by Method 625. Method 605 for the quantitative analysis of benzidine is provided in Section 7.2 of this Appendix. Gas chromatographic/mass spectral analysis may be used to substitute for the high performance liquid chromatography method cited in Method 605. However, all extraction and concentration techniques must be followed as per Method 605. This additional analysis, if required, must be completed within 20 days of sample receipt.

4. Since tetrachlorotoluene standards are not readily available and due to the poor resolution of the isomers of these compounds, tetrachlorotoluenes will only be qualitatively identified and reported.

5. Where compounds are detected which are not among those listed for quantitation, qualitative identification should be made according to the procedures entitled "Qualitative Analysis by GC/MS" which are contained in Section 7.6 of this Appendix.

B. Method B

Method 625, Base Neutrals, Acids and Pesticides, as described in the Federal Register, Volume 44, No. 233, 3 December 1979, and contained in Section 7.5 of this Appendix, is to be followed for this analysis with the following additions, deletions, and comments.

1. Method B is a variation on the standard Method 625 analysis procedure. The water sample is extracted, as in Method 625, first in a basic medium and then in an acid medium. Rather than the analysis of individual fractions by packed column GC/MS, Method B requires that the two extracts be individually analyzed using capillary GC/MS. Column specifications, chromatographic conditions, and mass spectrometer operation are as follows:

Column: 30 meter fused silica SE-54 wall coated open tubular capillary column.

Splitless Injection Parameters:

Injection mode: splitless

Sweep initiation: 30 seconds

Sweep flow: $\geq$ 12 ml/min

Column flow (He)
measured at atmospheric pressure: 1.0 ml/min

Interface:

Temperature: 265°C

Column directly coupled to source (no transfer lines)

Injection Volume:

1.0 μℓ with capillary style syringe

Temperature Program:

Initial: 30°C for 2 minutes

Program: ramp to 260°C at 10°C/min

Hold: 260°C, 15 minutes

Thermal gradients must be avoided for best analysis results. Phenomena such as "double peaking" do not constitute acceptable data. Particular attention to detail is required to ensure best results; this includes accurate reproduction of temperatures and injection techniques.

Mass Spectrometer Operation:

Electron energy - 70 volts

Mass range - 35 to 450 amu

Scan time - 1 second or less

2. Benzidine decomposes during the concentration and drying steps of Method 625; it may be observed, but the concentration measurements cannot be considered reliable and a second analysis must be performed if it is detected by Method 625. Method 605 for the quantitative analysis of benzidine is provided in Section 7.2 of this Appendix. Gas chromatographic/mass spectral analysis may be used to substitute for the high performance liquid chromatography method cited. However, all extraction and concentration techniques must be followed as per Method 605. This additional analysis must be completed within 20 days of sample receipt.

3. Since tetrachlorotoluene standards are not readily available, tetrachlorotoluene will only be qualitatively identified and reported.

4. Where compounds are detected which are not among those listed for quantitation, qualitative identification should be made according to the procedures detailed in Section 7.6 of this Appendix.

5. Quality control requirements for this analysis are given in Section 2.3.2 of this Appendix.

C. Method C

Method 625, Base Neutrals, Acids and Pesticides, as described in the Federal Register, Vol. 44, No. 233, 3 December 1979, and contained in Section 7.5 of this Appendix, is to be followed for the analysis of the compounds of interest with the following additions, deletions, and comments:

1. Method C uses the extraction scheme of Method 625 to produce a base-neutral and an acid fraction. Aliquots of each fraction are combined to make a third (combined) fraction. The combined fraction is then analyzed by capillary GC/MS using the following operation and performance specifications.

   Column: 30 meter fused silica SE-54 wall coated open tubular capillary column.

   Splitless Injection Parameters:

   Injection mode: splitless

   Sweep initiation: 30 seconds

   Sweep flow: $\geq$ 12 ml/min

   Column flow (He)
   measured at atmospheric pressure: 1.0 ml/min

   Interface:

   Temperature: 265°C

   Column directly coupled to source (no transfer lines)

   Injection Volume:

   1.0 µℓ with capillary style syringe

   Temperature Program:

   Initial: 30°C for 2 minutes

   Program: ramp to 260°C at 10°C/min

   Hold: 260°C, 15 minutes

   Note: Thermal gradients must be avoided for best analysis results. Phenomena such as "double peaking" do not constitute acceptable data. Particular attention to detail is required to ensure best results; this includes accurate reproduction of temperatures and injection techniques.

Mass Spectrometer Operation:

Electron energy - 70 volts

Mass range - 35 to 450 amu

Scan time - 1 second or less

2. Benzidine decomposes during the concentration and drying steps of Method 625; it may be observed, but the concentration measurements cannot be considered reliable and a second analysis must be performed if it is detected by Method 625. Method 605 for the quantitative analysis of benzidine is provided in Section 7.2 of this Appendix. Gas chromatographic/mass spectral analysis may be used to substitute for the high performance liquid chromatography method cited. However, all extraction and concentration techniques must be followed as per Method 605. This additional analysis must be completed within 20 days of sample receipt.

3. Since tetrachlorotoluene standards are not readily available, tetrachlorotoluene will only be qualitatively identified and reported.

4. Where compounds are detected which are not among those listed for quantitation, qualitative identification should be made according to the procedures detailed in Section 7.6 of this Appendix.

5. Quality control requirements for this analysis are given in Section 2.3.2 of this Appendix.

D. Method D

Method 625, Base Neutrals, Acids and Pesticides, as described in the Federal Register, Vol. 44, No. 233, December 3, 1979 and contained in Section 7.5 of this Appendix is to be followed for the analysis of the compounds of interest with the following additions, deletions and comments:

1. Method D uses the extraction scheme of Method 625 to produce a base/neutral and acid fraction; aliquots of each fraction are combined to make a third (combined) fraction. Each of the three fractions (base neutral, acid and combined) are then analyzed by capillary GC/MS according to the following operating and performance specifications:

   Column: 30 meter fused silica SE-54 wall coated open tubular capillary column.

   Splitless Injection Parameters:

   Injection mode: splitless

   Sweep initiation: 30 seconds

   Sweep flow: ≥ 12 ml/min

   Column flow (He) measured at atmospheric pressure: 1.0 ml/min

   Interface:

   Temperature: 265°C

   Column directly coupled to source (no transfer line)

   Injection Volume:

   1.0 μℓ with capillary style syringe

   Temperature Program:

   Initial: 30°C for 2 minutes

   Program: ramp to 260°C @ 10°C/min

   Hold: 260°C, 15 minutes

   Note: Thermal gradients must be avoided for best analysis results. Phenomena such as "double peaking" do not constitute acceptable data. Particular attention to detail is required to ensure best results. This includes accurate reproduction of temperatures and injection techniques.

Mass Spectrometer Operation:

Electron energy: 70 volts

Mass range: 35 to 450 amu

Scan time: 1 second or less

2. Benzidine decomposes during the concentration and drying steps of Method 625; it may be observed, but the concentration measurements cannot be considered reliable and a second analysis must be performed if it is detected by Method 625. Method 605 for the quantitative analysis of benzidine is provided in Section 7.2 of this Appendix. Gas chromatographic/mass spectral analysis may be used to substitute for the high performance liquid chromatography method cited. However, all extraction and concentration techniques must be followed as per Method 605. This additional analysis must be completed within 20 days of sample receipt.

3. Since tetrachlorotoluene standards are not readily available, tetrachlorotoluene will only be qualitatively identified and reported.

4. Where compounds are detected which are not among those listed for quantitation, qualitative identification should be made according to the procedures detailed in Section 7.6 of this Appendix.

5. Quality control requirements for this analysis are given in Section 2.3.2 of this Appendix.

2.3.2 Quality Control Procedures

Quality control procedures to be employed for the analysis of semivolatile organics in water are described below. Included are procedures specific to the analysis of benzidine and hexachlorocyclopentadiene. Requirements for instrument calibration and the frequency and types of internal QC samples to be run are discussed and summarized in Table 2-5. In addition, Table 2-5 gives control limits and corrective action for each activity.

A. Tuning of Mass Spectrometer

Daily measurements of the GC/MS standard reference compound decafluorotriphenylphosphine (DFTPP) and/or 4-bromofluorobenzene (BFB) must be made. The procedures and criteria to be met for DFTPP are as set forth in Method 625. The procedure for BFB is injection of 50 nanograms of 4-bromofluorobenzene into the gas chromatograph with the following acceptance criteria applying:

Mass	Ion Abundance Criteria
50	15-40% of the base peak
75	30-60% of the base peak
95	base peak, 100% relative abundance
96	5-9% of the base peak
173	less than 1% of the base peak
174	greater than 50% of the base peak
175	5-9% of mass 174
176	greater than 50% of the base peak
176	greater than 94% but less than 100% of 174
177	5-9% of mass 175

The specified criteria must be met prior to the analysis of samples each analysis day. This data must be recorded and provided to the Prime Contractor.

B. Calibration of GC/MS System

The GC/MS system must be initially calibrated to determine response factors using standards as described in Section 6 of Method 625. After the system has been calibrated, the calibration for organic compounds must be verified at least once each day of running (8 hours) by the use of standards containing the internal standard(s). If the deviation is greater than 20 percent, the system must be recalibrated. Information regarding the verification of calibration should be provided to the Prime Contractor.

C. Internal Standards

Internal standards are added to each sample according to the procedures outlined in Section 6.4 of Method 625. The compounds used as internal standards for the analysis of semivolatile organics in water are the following:

anthracene d_{10}

naphthalene d_8

chrysene d_{12}

TABLE 2-5. INTERNAL QC REQUIREMENTS--SEMIVOLATILES IN WATER

Operation check	Frequency	Control limits	Corrective action planned
Tuning of mass spectrometer	Daily before analysis of samples	Table 10 of Method 625[a]	Retune spectrometer
Verify capillary column performance[b]	Daily prior to analysis of samples	Tailing factor ≤ 1.5	Check analytical procedure Analyze second reference sample Replace column
Method blank (reagent water)	Daily before analysis batch[c]/ analysis day	No significant concentrations found	Check analytical procedure
Calibration check of GC/MS system	Once per 8 hours of analysis time	Deviation less than ±20 percent	Recalibrate system
Internal standards	Added to each sample	Deviation less than ±20 percent	Check analytical procedure Analyze reference sample Invalidate results
Surrogate compounds	Added to each sample	As specified in text	Check analytical procedure Analyze reference sample Invalidate results
Laboratory control standard (LCS)	One per analysis batch[c]/ analysis day	As specified in text	Check analytical procedure Analyze second reference sample Invalidate results
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

[a] A copy of Method 625 appears in Section 7.5 of this Appendix.

[b] Pertains to analysis Methods B, C, and D.

[c] Analysis batch = group of samples processed as a set, usually containing 15 samples or less.

D. Surrogate Compounds

Surrogate organic compounds will be added at a known concentration of 5-25 µg/l to every environmental sample. The analytical performance, expressed as a percentage of the true values for these compounds, will be monitored with the control limits given below indicating acceptable performance. The surrogate compounds for semivolatiles in water are the following:

Compound	Control limits
2-fluorophenol	18-58%
1-fluoronaphthalene	33-88%
4,4'-dibromooctafluorobiphenyl	34-98%

E. Laboratory Control Standards (LCS)

Laboratory control standard (LCS) will be employed to identify systematic method and operator errors. The LCS is a mixture of a number of compounds of known concentration in a reference material or spiked into reagent water. A minimum of the compounds to be used to make up the LCS for semivolatile organic analyses are given below. One LCS must be processed through the entire analytical method for each set of samples extracted in a group at the same time on the same day. Normally there will be one LCS for every 5-15 samples depending on how many samples are extracted in a given batch.

Standards for base/neutrals and acids LCS should be prepared at a concentration in the range of 5-25 µg/l using either EMSL-Cincinnati QC concentrates or standards supplied by the individual laboratory. The minimum standard compounds to be used and control limits expressed as percentage of true values are as follows:

Compound	Control limits
Method 625 (A, B, C, D)	
1,4-dichlorobenzene	16-64%
1,2,4-trichlorobenzene	36-96%
1,2,3,4-tetrachlorobenzene	35-59%
Fluoranthene	40-118%
2,4,6-trichlorophenol	46-82%
2-chloronaphthalene	34-98%
2,6-dinitrotoluene	34-94%
4-nitrophenol	36-68%
2-fluorophenol	18-58%
Pentachlorophenol	63-111%
Beta-benzenehexachloride	19-119%
1-fluoronaphthalene	33-81%
4,4-dibromobiphenyl	36-94%
4,4-dibromooctafluorobiphenyl	34-98%
Di-m-butylphthalate	45-125%

Compound	Control limits
Method 605	
Benzidine	To be determined
Other	
Hexachlorocyclopentadiene	To be determined

A control chart should be maintained for each of the analytes.

F. Method Blanks

One method blank (reagent water) must be processed through the entire laboratory analytical procedure for each set of samples extracted in a group at the same time on the same day. Normally this will be one method blank for every 5 to 15 samples depending on how many samples are extracted in a given batch. The method blank must not show any signals that correspond to compounds on the Love Canal or priority pollutants list. If common laboratory contaminants, e.g., phthalate esters, are found in the method blanks, reported values for the same compounds in the environmental samples must be reduced by the amount found in the blank.

G. Replicate Analyses

Intralaboratory precision of the environmental measurements will be evaluated by the measurement of one duplicate (split) of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method.

H. Capillary Column Performance

The performance of the capillary chromatographic column used in Methods B, C, and D must be verified daily before analysis by injection of known mixtures. A tentative procedure for this performance test is as follows:

- 100 ng pentachlorophenol and benzidine simultaneously using a 1.0 μl injection.
- Analysis of the Grob mixture.
- Criterion: Tailing factor ≤ 1.5 for these compounds.

2.4 PESTICIDES

2.4.1 Analytical Procedure

Procedures for the analysis of pesticides and PCBs are those stated in Method 608, Federal Register, December 3, 1979. A copy of this procedure is included in Section 7.3 of this Appendix. The following modification to Method 608 will be observed for all water analyses:

> All pesticide species positively identified by Method 608 gas chromatographic procedures (GC/ECD) shall be further verified by GC/MS using the appropriate portion of Method 625 (pages 69540-69552, Federal Register, December 3, 1979) provided the necessary GC/MS detection limit criteria have been met. A copy of Method 625 can be found in Section 7.5 of this Appendix.

Preservation of water samples for pesticides analysis should have been performed in the field and noted on the analysis tag for each type of sample as follows:

Sample type	Preservative	Amount
Drinking water	10N NaOH or 1:1 H_2SO_4	pH 5-9
Groundwater	10N NaOH or 1:1 H_2SO_4	pH 5-9
Sump, sewer, drain and surface waters	10N NaOH or 1:1 H_2SO_4	pH 5-9

All samples must be maintained at 4°C until analysis.

2.4.2 Quality Control Procedures

The quality control procedures to be utilized in these analyses are those described in Method 608. Calibration and standardization procedures for the gas chromatograph are sufficiently described in Section 6 of Method 608 and will not be further discussed in this section. Requirements for analysis of method blanks, replicates, and known QC samples are described below. The frequency, control limits, and corrective action for each item are summarized in Table 2-6.

A. Method Blanks

One method blank (reagent water) must be processed through the entire laboratory analytical procedure for each set of samples extracted in a group at the same time on the same day. Normally this will be one method blank for every 5 to 15 samples, depending on how many samples are extracted in a given batch. The method blank must not show any signals that correspond to compounds on the Love Canal or priority pollutants list. If common laboratory contaminants; e.g., phthalate esters, are found in the method blanks, reported values for the same compounds in the environmental samples must be reduced by the amount found in the blank.

B. Laboratory Control Standards (LCS)

Laboratory control standards (LCS) will be employed to identify systematic method and operator errors. The LCS is a concentrate of one or more compounds of known concentration in a reference material or spiked into reagent water.

Presently, the LCS for pesticides in water must consist of (at a minimum) 5-25 μg/l of Aroclor 1242. Control limits for this compound have not yet been established. One LCS must be processed through the entire analytical method for each set of samples extracted in a group at the same time on the same day. Normally there will be one LCS for every 5 to 15 samples, depending on how many samples are extracted in a given batch. Results of LCS analysis are to be recorded on the appropriate data sheets and must include measured and expected concentration for each component of the LCS.

C. Replicate Analyses

Intralaboratory precision of the environmental measurements will be evaluated by the measurement of one duplicate (split) of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method.

TABLE 2-6. INTERNAL QC REQUIREMENTS — PESTICIDES IN WATER

Operation check	Frequency	Control limits	Corrective action planned
Method blank (reagent water)	One per analysis batch[a]/ analysis day	No significant concentrations found	Correct for blank Check analytical procedure
Laboratory control standard (LCS)	One per analysis batch[a]/ analysis day	To be determined	Check analytical procedure Analyze second reference sample Invalidate results
Confirm identified pesticides by Method 625 (GC/MS)	All samples	Identification confirmed	Analyze replicate aliquot by Method 608 Invalidate original Method 608 result
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

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[a] Analysis batch = group of samples processed as a set, usually containing 15 samples or less.

2.5 METALS

2.5.1 Analytical Procedures

The analysis of metals in water samples is performed using Inductively Coupled Plasma (ICP) and/or Atomic Absorption Spectroscopy (AAS). The applicability of each technique to the various metals of interest is detailed in the analytical procedures which follow. Since specialized procedures are required for preparation and analysis of selenium and mercury, these elements are presented individually. Section 2.5.1 is therefore organized as follows:

A. Inductively Coupled Plasma

B. Atomic Absorption Spectroscopy

C. Mercury

D. Selenium

Detection limits which must be met in the analysis of metals in water are given in Table 2-7.

TABLE 2-7. REQUIRED DETECTION LIMITS

Element	Required detection limit (μg/l)
Arsenic	53
Antimony	32
Barium	2
Beryllium	0.3
Cadmium	4
Chromium	7
Copper	6
Lead	42
Mercury	2
Nickel	15
Selenium	10
Silver	7
Thallium	40
Zinc	2

Field preservation of all water samples for metals analysis consists of adjusting the sample pH to less than 2 using 1:1 Ultrex HNO_3. This preservation, if performed, should be noted on the analysis tag. If such notation has not been made, check sample pH and adjust to pH <2 with 1:1 Ultrex HNO_3. Document acidification and time performed. Wait four (4) hours before analyzing to ensure dissolution of metals. Samples are shipped and stored in glass containers and maintained at 4°C until analysis.

A. Inductively Coupled Plasma

If water analysis is performed by ICP, the methods and techniques described in "Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes," EMSL-Cincinnati, July 1980, are to be followed for this analysis with the following additions, deletions, and comments:

1. This method, which begins on page 4 of this section, may be used for the analysis of antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, nickel, silver, thallium, and zinc in water.

2. The digestion procedure outlined in paragraph 8.4, "Total Recoverable Elements," should be used for the preparation of all samples.

3. The sample must be concentrated to one-fifth of the original volume prior to analysis in order to achieve the desired reporting levels of Table 2-7.

4. Specific quality control procedures for these analyses are outlined in Section 2.5.2.

B. Atomic Absorption Spectroscopy (AAS)

If water analysis is performed by AAS, the methods and techniques described in "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, are to be followed for this analysis with the additions, deletions, and comments noted below. The standard AAS methods are given in Section 7.8 of this Appendix.

1. This method may be used for the analyses of antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, nickel, silver, thallium, and zinc in water.

2. The digestion procedure stated in paragraph 8.4 of "Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes," EMSL-Cincinnati, July 1980, is suitable for all elements except arsenic; a copy of the ICP procedure is contained in this section of this Appendix.

3. Samples to be analyzed for arsenic should be prepared according to the procedures stated in Method 206.2 of "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, which appears in Section 7.8 of this Appendix.

4. Quality control procedures specific to these analyses are given in Section 2.5.2 of this Appendix.

C. Mercury by Cold Vapor Technique

Mercury analysis is performed according to the procedures stated in Method 245.1 or Method 245.2 of "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020; these methods are given in Section 7.8 of this Appendix.

Quality control procedures specific to this analysis are given in Section 2.5.2 of this Appendix.

D. Selenium

The procedures outlined in Method 270.2 of "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, are to be followed for this analysis. A copy of this procedure is given in Section 7.8 of this Appendix.

Quality control procedures specific to this analysis are given in Section 2.5.2 of this Appendix.

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

INTERIM

U.S. ENVIRONMENTAL PROTECTION AGENCY
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

July 1980

Foreword

This method has been prepared bvy the staff of the Environmental Monitoring and Support Laboratory - Cincinnati, with the cooperation of the EPA-ICP Users Group. Their cooperation and support is gratefully acknowledged.

This method represents the current state-of-the-art, but as time progresses, improvements are anticipated. Users are encouraged to identify problems and assist in updating the method by contacting the Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268.

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interference are taken into account. This is especially true when dissolved solids exceed 1500 mg/l. (See 4.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See 4.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

Table 1 - Recommended Wavelengths(1) and Estimated Instrumental Detection Limits

Element	Wavelength, nm	Estimated detection limit, μg/l(2)
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	see(3)
Selenium	196.026	75
Silica (SiO_2)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

(1) The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 4.1.1).

(2) The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

(3) Highly dependent on operating conditions and plasma position.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled argon plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines of samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 4.1 (and tests for their presence as described in 4.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 Dissolved--Those elements which will pass through a 0.45 μm membrane filter.

3.2 Suspended--Those elements which are retained by a 0.45 µm membrane filter.

3.3 Total--The concentration determined on an unfiltered sample following vigorous digestion (Section 8.3), or the sum of the dissolved plus suspended concentrations. (Section 8.1 plus 8.2.)

3.4 Total recoverable--The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 8.4).

3.5 Instrumental detection limit--The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 Sensitivity--The slope of the analytical curve, i.e., functional relationship between emission intensity and concentration.

3.7 Instrument check standard--A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 6.6.1)

3.8 Interference check sample--A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 6.6.2)

3.9 Quality control sample--A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 6.6.3)

3.10 Calibration standards--a series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 6.4)

3.11 Linear dynamic range--The concentration range over which the analytical curve remains linear.

3.12 Reagent blank--A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 6.5.2)

3.13 Calibration blank--A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 6.5.1)

3.14 Method of standard addition--The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 9.6.1)

4. Interferences

4.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

4.1.1 Spectral interferences can be categorized as 1) overlap of a spectral line from another element; 2) unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination phenomena; and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multielement instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

The interference information, which was collected at the Ames Laboratory,[1] is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/l of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/l of aluminum. According to Table 2, 100 mg/l of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/l. Therefore, 10 mg/l of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/l. The reader is cautioned that other analytical systems may exhibit somewhat

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[1] Ames Laboratory, USDOE, Iowa State University, Ames Iowa 50011

Table 2. Analyte Concentrations Equivalents (mg/l) Arising From Interferents at the 100 mg/l Level

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system.

Only those interferences listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

4.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon prior

Table 3. Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table 2.

Analytes	(mg/l)
Al	10
As	10
B	10
Ba	1
Be	1
Ca	1
Cd	10
Co	1
Cr	1
Cu	1
Fe	1
Mg	1
Mn	1
Mo	10
Na	10
Ni	10
Pb	10
Sb	10
Se	10
Si	1
Tl	10
V	1
Zn	10

Interferents	(mg/l)
Al	1000
Ca	1000
Cr	200
Cu	200
Fe	1000
Mg	1000
Mn	200
Ni	200
Ti	200
V	200

to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

4.1.3 Chemical Interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

4.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 4.2.1 through 4.2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values.

4.2.1 Serial dilution--If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit (13.3) that has been established for that matrix.) If not, a chemical or physical interference effect should be suspected.

4.2.2 Spike addition--The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

Caution: The standard addition technique does not detect coincident spectral overlap. If suspected, use of an alternate wavelength or comparison with an alternate method is recommended (See 4.2.3).

4.2.3 Comparison with alternate method of analysis--When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

4.2.4 Wavelength scanning of analyte line region--If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

5. Apparatus

5.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

5.1.1 Computer controlled atomic emission spectrometer with background correction.

5.1.2 Radiofrequency generator.

5.1.3 Argon gas supply, welding grade or better.

5.2 Operating conditions -- Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

6. Reagents and standards

6.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

6.1.1 Acetic acid, conc. (sp gr 1.06).

6.1.2 Hydrochloric acid, conc. (sp gr 1.19)

6.1.3 Hydrochloric acid, (1+1): Add 500 ml conc. HCl (sp gr 1.19) to 400 ml deionized, distilled water and dilute to 1 liter.

6.1.4 Nitric acid, conc. (sp gr 1.41).

6.1.5 Nitric acid, (1+1): Add 500 ml conc. HNO_3 (sp gr 1.41) to 400 ml deionized, distilled water and dilute to 1 liter.

6.2 Deionized, distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (13.6).

6.3 Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 h at 105°C unless otherwise specified.
(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.)
Typical stock solution preparation procedures follow:

6.3.1 Aluminum solution, stock, 1 ml = 100 µg Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 ml of (1+1) HCl and 1 ml of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 ml of (1+1) HCl and dilute to 1,000 ml with deionized, distilled water.

6.3.2 Antimony solution stock, 1 ml = 100 µg Sb: Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in deionized distilled water, add 10 ml (1+1) HCl and dilute to 1000 ml with deionized, distilled water.

6.3.3 Arsenic solution, stock. 1 ml = 100 µg As: Dissolve 0.1320 g of As_2O_3 in 100 ml of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.4 Barium solution, stock, 1 ml = 100 µg Ba: Dissolve 0.1516 g $BaCl_2$ (dried at 250°C for 2 hrs) in 10 ml deionized, distilled water with 1 ml (1+1) HCl. Add 10.0 ml (1+1) HCl and dilute to 1,000 ml with deionized, distilled water.

6.3.5 Beryllium solution, stock, 1 ml = 100 µg Be: Do not dry. Dissolve 1.966 g $BeSO_4 : 4H_2O$, in deionized, distilled water, add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.6 Boron solution, stock. 1 ml = 100 µg B: Do not dry. Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water and dilute to 1,000 ml. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

6.3.7 Cadmium solution, stock, 1 ml = 100 µg Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.8 Calcium solution, stock, 1 ml = 100 µg Ca: Suspend 0.2498 g $CaCO_3$ dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.9 Chromium solution, stock, 1 ml = 100 µg Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete, acidify with 10 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.10 Cobalt solution, stock. 1 ml = 100 µg Co: Dissolve 0.1000 g of cobalt in a minimum amount of (1+1) HNO_3. Add 10.0 ml (1+1) HCl and dilute to 1,000 ml with deionized, distilled water.

6.3.11 Copper solution, stock. 1 ml = 100 µg Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.12 Iron solution, stock, 1 ml = 100 µg Fe: Dissolve 0.1430 g Fe_2O_3 in 10 ml deionized, distilled water with 1 ml (1+1) HCl. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.13 Lead solution, stock, 1 ml = 100 µg Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.14 Magnesium solution, stock. 1 ml = 100 µg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.15 Manganese solution, stock, 1 ml = 100 µg Mn: Dissolve 0.1000 g of manganese metal in the acid mixture 10 ml conc. HCl and 1 ml conc. HNO_3, and dilute to 1,000 ml with deionized, distilled water.

6.3.16 Molybdenum solution, stock, 1 ml = 100 µg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1,000 ml.

6.3.17 Nickel solution, stock, 1 ml = 100 µg Ni: Dissolve 0.1000 g of nickel metal in 10 ml hot conc. HNO_3, cool and dilute to 1,000 ml with deionized, distilled water.

6.3.18 Potassium solution, stock. 1 ml = 100 µg K: Dissolve 0.1907 g KCl, dried at 110°C, in deionized, distilled water dilute to 1,000 ml.

6.3.19 Selenium solution, stock, 1 ml = 100 µg Se: Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 ml.

6.3.20 Silica solution, stock, 1 ml = 100 µg SiO_2: Do not dry. Dissolve 0.4730 g $Na_2SiO_3 \cdot 9H_2O$ in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.21 Silver solution, stock, 1 ml = 100 µg Ag: Dissolve 0.1575 g $AgNO_3$ in 100 ml of deionized, distilled water and 10 ml conc. HNO_3. Dilute to 1,000 ml with deionized, distilled water.

6.3.22 Sodium solution, stock, 1 ml = 100 µg Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.23 Thallium solution, stock, 1 ml = 100 µg Tl: Dissolve 0.1303 g $TlNO_3$ in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.24 Vanadium solution, stock, 1 ml = 100 µg V: Dissolve 0.2297 g NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.25 Zinc solution, stock, 1 ml = 100 µg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.4 Mixed calibration standard solutions--Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 6.4.1 thru 6.4.5). Add 2 ml of (1+1) HNO_3 and 10 ml of (1+1) HCl and dilute to 100 ml with deionized, distilled water. (See notes 1 and 6). Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or impurity contamination. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (See 6.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

6.4.1 Mixed standard solution I--Manganese, beryllium, cadmium, lead, and zinc.

6.4.2 Mixed standard solution II--Barium, copper, iron, vanadium, and cobalt.

6.4.3 Mixed standard solution III--Molybdenum, silica, arsenic, and selenium.

6.4.4 Mixed standard solution IV--Calcium, sodium, potassium, aluminum, chromium and nickel.

6.4.5 Mixed standard solution V--Antimony, boron, magnesium, silver, and thallium.

NOTE 1: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 ml of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 ml with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/l. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

6.5 Two types of blanks are required for the analysis. The calibration blank (3.13) is used in establishing the analytical curve while the reagent blank (3.12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

6.5.1 The calibration blank is prepared by diluting 2 ml of (1+1) HNO_3 and 10 ml of (1+1) HCl to 100 ml with deionized, distilled water. (See note 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.

6.5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

6.6 In addition to the calibration standards, an instrument check standard (3.7), an interference check sample (3.8) and a quality control sample (3.9) are also required for the analyses.

6.6.1 The instrument check standard is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. (See 11.1.1.)

6.6.2 The interference check sample is prepared by the analyst in the following manner. Select a representative sample which contains minimal concentrations of the analytes of interest but known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at either 100 µg/l or 5 times the estimated detection limits given in Table 1 which ever is larger. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample will be available from the Quality Assurance Branch of EMSL-Cincinnati. (See 11.1.2).

6.6.3 The quality control sample should be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal equality can be procured. (See 11.1.3.)

7. Sample handling and preservation

7.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through absorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order (See notes 2 and 3).

NOTE 2: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

NOTE 3: If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

7.2 Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

7.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45-µm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50-100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 ml of (1+1) acid per liter should be sufficient to preserve the sample.

7.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45-µm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

7.2.3 For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferably at the time of collection. The sample is not filtered before processing.

8. Sample Preparation

8.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. (See Note 6.) If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described in 8.3.

8.2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 250-ml Griffin beaker and add 3 ml conc. HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 ml of conc. HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (1 to 2 ml), cool, add 10 ml HCl (1+1) and 15 ml deionized, distilled water per 100 ml dilution and warm the beaker gently for 15 min to dissolve any precipitated or residue material. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

NOTE 4: In place of filtering, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

8.3 For the determination of total elements, choose a measured, volume of the well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See note 5.) Add 3 ml of conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil. Cool the beaker and add another 3 ml portion of conc. HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness (1 to 2 ml) and cool the beaker. Add 10 ml of 1+1 HCl and 15 ml of deionized, distilled water per 100 ml of final solution and warm the beaker gently for 15 min. to dissolve any precipitate or residue resulting from evaporation. Allow to cool, wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See note 4). Adjust the sample to a predetermined volume based on the expected concentrations of elements present. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

NOTE 5: If low determinations of boron are critical, quartz glassware should be used.

NOTE 6: If the sample analysis solution has a different acid concentration from that given in 8.3 and 8.4, but does not introduce a physical interference or affect the analytical result, the same calibration standard may be used.

8.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 2 ml of (1+1) HNO_3 and 10 ml of (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 ml making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume to 100 ml and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

9. Procedure

9.1 Set up instrument with proper operating parameters established in Section 5.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

9.2 Initiate appropriate operating configuration of computer.

9.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 6.4. Flush the system with the calibration blank (6.5.1) between each standard. (See note 7.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE 7: For boron concentrations greater than 500 µg/l extended flush times of 1 to 2 minutes may be required.

9.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than ± 5 percent (or the established control limits whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

9.5 Begin the sample run flushing the system with the calibration blank solution (6.5.1) between each sample. (See Note 9.) Analyze the instrument check standard (6.6.1) and the calibration blank (6.5.1) each 10 samples.

9.6 If it has been found that methods of standard addition are required, the following procedure is recommended.

9.6.1 The standard addition technique (13.2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the solvent.

The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$c_x = \frac{S_B V_s c_s}{(S_A - S_B)\ V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

10. Calculation

10.1 Reagent blanks (6.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

10.2 If dilutions were performed, the appropriate factor must be applied to sample values.

11.1.3 A quality control sample (6.6.3) obtained from an outside source must first be used for the initial verification of the calibration standards. A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the results are not within ± 5% of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

12. Precision and Accuracy

12.1 In an EPA round robin phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 4 lists the true value, the mean reported value and the mean % relative standard deviation.

Table 4. ICP) Precision and Accuracy Data

Element	Sample # 1			Sample # 2			Sample # 3		
	True Value µg/1	Mean Reported Value µg/1	Mean Percent RSD	True Value µg/1	Mean Reported Value µg/1	Mean Percent RSD	True Value µg/1	Mean Reported Value µg/1	Mean Percent RSD
Be	750	733	0.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

Not all elements were analyzed by all laboratories.

13. References

13.1 Winge, R. K., V. J. Peterson, and V. A. Fassel, "Inductively Coupled Plasma-Atomic Emission Spectroscopy: Prominent Lines, EPA-600/4-79-017.

13.2 Winefordner, J. D., "Trace Analysis: Spectroscopic Methods for Elements," Chemical Analysis. Vol. 46, pp. 41-42.

13.3 Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019.

13.4 Garbarino, J. R. and Taylor, H. E., "An Inductively-Coupled Plasma Atomic Emission Spectrometric Method for Routine Water Quality Testing," Applied Spectroscopy 33, No. 3(1979).

13.5 "Methods for Chemical Analysis of Water and Wastes." EPA-600/4-79-020.

13.6 Annual Book of ASTM Standards, Part 31.

2.5.2 Quality Control Procedures

Instrumental quality control procedures are included in the analytical methods. Additional quality control procedures such as the use of method blanks and laboratory control standards are described in some detail below, and the frequency, control limits and corrective action for each summarized in Table 2-8.

A. Sample Spiking

For analysis by AAS and ICP, the first 10 samples from each type (drinking water, sump water, surface water, and ground water) must be spiked at the concentration level shown below. If recoveries for these spikes are between 85 and 115 percent, then one of each of the next 20 samples of each type must be spiked. The measured recoveries of these additional spikes must also fall within 85 to 115 percent. If the percent recoveries are not within these limits, the method of standard additions as prescribed in Metals-12 from "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 and included in Section 7.8 of this Appendix must be used for analyses on all samples of that type.

Constituent	Spike concentration mg/1*
Arsenic	0.05
Antimony	0.25
Barium	1.0
Beryllium	0.015
Cadmium	0.01
Chromium	0.05
Lead	0.05
Mercury	0.002
Nickel	0.15
Selenium	0.01
Silver	0.05
Thallium	1.0
Zinc	5.0

B. Laboratory Control Standards

For all methods, laboratory control standards (LCS) shall be employed to monitor systematic method and operator errors. The LCS is a solution of one or more analyses of known concentration in reagent water. Separate LCSs will

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*Spike levels are prior to concentrating.

TABLE 2-8. INTERNAL QC REQUIREMENTS--METALS IN WATER

Operation check	Frequency	Control limits	Corrective action planned
Method blank (reagent water)	One per analysis batch[a]/ analysis day	No significant concentrations found	Correct for blank Check analytical procedure
Laboratory control standard (LCS)	One per analysis batch[a]/ analysis day	As specified in text	Check analytical procedure Analyze second reference sample Invalidate results
Spiked samples (initial study)	First 10 of each type of water sample	Recovery 85-115% of each added element	Use standard additions method to quantitate water samples of that type.[b]
Spiked samples (check)	If control limits of above are met, one of the next 20 water samples of each type.	Recovery 85-115% of each added element	Use standard additions method to quantitate water samples of that type.[b]
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

[a] Analysis batch = group of samples processed as a set, usually containing 15 samples or less.

[b] Metals 12 from EPA-600/4-79-020, reproduced in Section 7.8 of this Appendix.

be used for each method, and each will be prepared using either EMSL-Cincinnati quality control concentrates or standards supplied by the individual laboratory. The analytes which must be included, as a minimum, along with the required concentration range are shown below. One LCS must be processed through the entire analytical method for each set of samples processed in a group at the same time on the same day. Normally, this will be one LCS for every 5 to 15 samples depending on how many samples are processed in a given batch. A control chart should be maintained for each of the analytes. The control limits to be used are also shown.

All measurements of LCS analytes must be expressed in terms of the percentage of true values, and these must be compared with the control limits. Any value that fails beyond the control limits shall trigger an investigation to determine the cause of the deviation and a correction of the problem. Values of environmental measurements from samples processed during that same work shift must be remeasured or not reported unless a satisfactory justification is prepared.

Minimum Analytes for Laboratory Control
Standards and Control Limits

Analyte	Control limits
ICP or AAS Methods	
Arsenic (≈0.3 mg/l)	89-111%
Antimony (≈0.5 mg/l)	90-110%
Barium (≈1.0 mg/l)	95-105%
Beryllium (≈0.5 mg/l)	95-105%
Cadmium (≈0.07 mg/l)	95-105%
Chromium (≈0.25 mg/l)	95-105%
Lead (≈0.4 mg/l)	92-108%
Nickel (≈0.3 mg/l)	96-104%
Silver (≈0.05 mg/l)	92-108%
Thallium (≈0.05 mg/l)	90-110%
Zinc (≈0.4 mg/l)	96-104%
Method 245.1 or 245.2	
Mercury (1 to 5 μg/l)	65-110%
Method 270.2	
Selenium (5 to 20 μg/l)	92-108%

C. Method Blanks

For all methods, one method blank (reagent water) must be processed through the entire laboratory analytical procedure for each set of samples processed in a group at the same time on the same day. Normally, this will be one method for every 5 to 15 samples depending on how many samples are in a given batch. If common laboratory contaminants are found in the method blanks and it is judged that the same contaminants are present in the environmental samples, reported values for these analyses must be reduced by the amount found in the blank.

D. Replicate Analyses

For all methods, intralaboratory precision of the environmental measurements must be evaluated by the measurement of one duplicate of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These data must be reported with the laboratory results and will be used by EPA in assessing the overall precision of the data.

2.6 ANIONS (FLUORIDE, NITRATE)

2.6.1 Analytical Procedures

The anions fluoride and nitrate are measured in water samples using standard procedures from "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020. For each anion, either of two methods is approved for these analyses.

Field preservation of all water samples for the analysis of fluoride and nitrate consists of the addition of 2 milliliters of concentrated H_2SO_4 to each liter of sample. These anion samples are shipped and stored in polyethylene containers and maintained at 4°C until analysis.

A. Fluoride

Either of the following procedures, both of which are reproduced in this section, may be used for the analysis of fluoride:

- Method 340.1 (Colorimetric, SPADNS with Bellack Distillation)
- Method 340.2 (Potentiometric, Ion Selective Electrode)

B. Nitrate

Either of the following procedures, both of which are reproduced in this section, may be used for the analysis of nitrate:

- Method 353.2 (Colorimetric, Automated Cadmium Reduction)
- Method 353.3 (Spectrophotometric, Cadmium Reduction)

FLUORIDE, TOTAL

Method 340.1 (Colorimetric, SPADNS with Bellack Distillation)

STORET NO. Total 00951
Dissolved 00950

1. Scope and Application
   1.1 This method is applicable to the measurement of fluoride in drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The method covers the range from 0.1 to about 2.5 mg/1 F. This range may be extended to 1000 mg/1 using the Fluoride Ion Selective Electrode Method (340.2) after distillation.
2. Summary of Method
   2.1 Following distillation to remove interferences, the sample is treated with the SPADNS reagent. The loss of color resulting from the reaction of fluoride with the zirconyl-SPADNS dye is a function of the fluoride concentration.
3. Comments
   3.1 The SPADNS reagent is more tolerant of interfering materials than other accepted fluoride reagents. Reference to Table 414:1, p 388, Standard Methods for the Examination of Waters and Wastewaters, 14th Edition, will help the analyst decide if distillation is required. The addition of the highly colored SPADNS reagent must be done with utmost accuracy because the fluoride concentration is measured as a difference of absorbance in the blank and the sample. A small error in reagent additon is the most prominent source of error in this test.
   3.2 Care must be taken to avoid overheating the flask above the level of the solution. This is done by maintaining an even flame entirely under the boiling flask.
4. Apparatus
   4.1 Distillation apparatus: A 1-liter round-bottom, long-necked pyrex boiling flask, connecting tube, efficient condenser, thermometer adapter and thermometer reading to 200°C. All connections should be ground glass. Any apparatus equivalent to that shown in Figure 1 is acceptable.
   4.2 Colorimeter: One of the following
      4.2.1 Spectrophotometer for use at 570 nm providing a light path of at least 1 cm.
      4.2.2 Filter photometer equipped with a greenish yellow filter having maximum transmittance at 550 to 580 nm and a light path of at least 1 cm.
5. Reagents
   5.1 Sulfuric acid, H_2SO_4, conc.

Approved for NPDES and SDWA
Issued 1971
Editorial revision 1974 and 1978

5.2 Silver sulfate, Ag_2SO_4 crystals.

5.3 Stock fluoride solution: Dissolve 0.221 g anhydrous sodium fluoride, NaF, in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.1 mg F.

5.4 Standard fluoride solution: Place 100 ml stock fluoride solution (5.3) in a 1 liter volumetric flask and dilute to the mark with distilled water; 1.00 ml = 0.010 mg F.

5.5 SPADNS solution: Dissolve 0.958 g SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, in distilled water in a 500 ml volumetric flask and dilute to the mark. Stable indefinitely if protected from direct sunlight.

5.6 Zirconyl-acid reagent: Dissolve 0.133 g zirconyl chloride octahydrate, $Zr0Cl_2 \cdot 8H_2O$ in approximately 25 ml distilled water in a 500 ml volumetric flask. Add 350 ml conc HCl and dilute to the mark with distilled water.

5.7 Acid-zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution (5.5) and zirconyl-acid reagent (5.6). The combined reagent is stable for at least 2 years.

5.8 Reference solution: Add 10 ml SPADNS solution (5.5) to 100 ml distilled water. Dilute 7 ml conc HCl to 10 ml and add to the dilute SPADNS solution. This solution is used for zeroing the spectrophotometer or photometer. It is stable and may be used indefinitely.

5.9 Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ in distilled water in a 1-liter volumetric flask and dilute to the mark with distilled water (CAUTION: Toxic-avoid ingestion).

6. Procedure

6.1 Preliminary distillation

6.1.1 Place 400 ml distilled water in the distilling flask.

6.1.2 Carefully add 200 ml conc. H_2SO_4 and swirl until contents are homogeneous.

6.1.3 Add 25 to 35 glass beads, connect the apparatus (Figure 1) making sure all joints are tight.

6.1.4 Heat slowly at first, then as rapidly as the efficiency of the condenser will permit (distillate must be cool) until the temperature of the flask contents reaches exactly 180°C. Discard the distillate. This process removes fluoride contamination and adjusts the acid-water ratio for subsequent distillations.

6.1.5 Cool to 120°C or below.

6.1.6 Add 300 ml sample, mix thoroughly, distill as in 6.1.4 until temperature reaches 180°C. Do not heat above 180°C to prevent sulfate carryover.

6.1.7 Add Ag_2SO_4 (5.2) at a rate of 5 mg/mg Cl when high chloride samples are distilled.

6.1.8 Use the sulfuric acid solution in the flask repeatedly until the contaminants from the samples accumulate to such an extent that recovery is affected or interferences appear in the distillate. Check periodically by distilling standard fluoride samples.

6.1.9 High fluoride samples may require that the still be flushed by using distilled water and combining distillates.

6.2 Colorimetric Determination:

6.2.1 Prepare fluoride standards in the range 0 to 1.40 mg/1 by diluting appropriate quantities of standard fluoride solution (5.4) to 50 ml with distilled water.

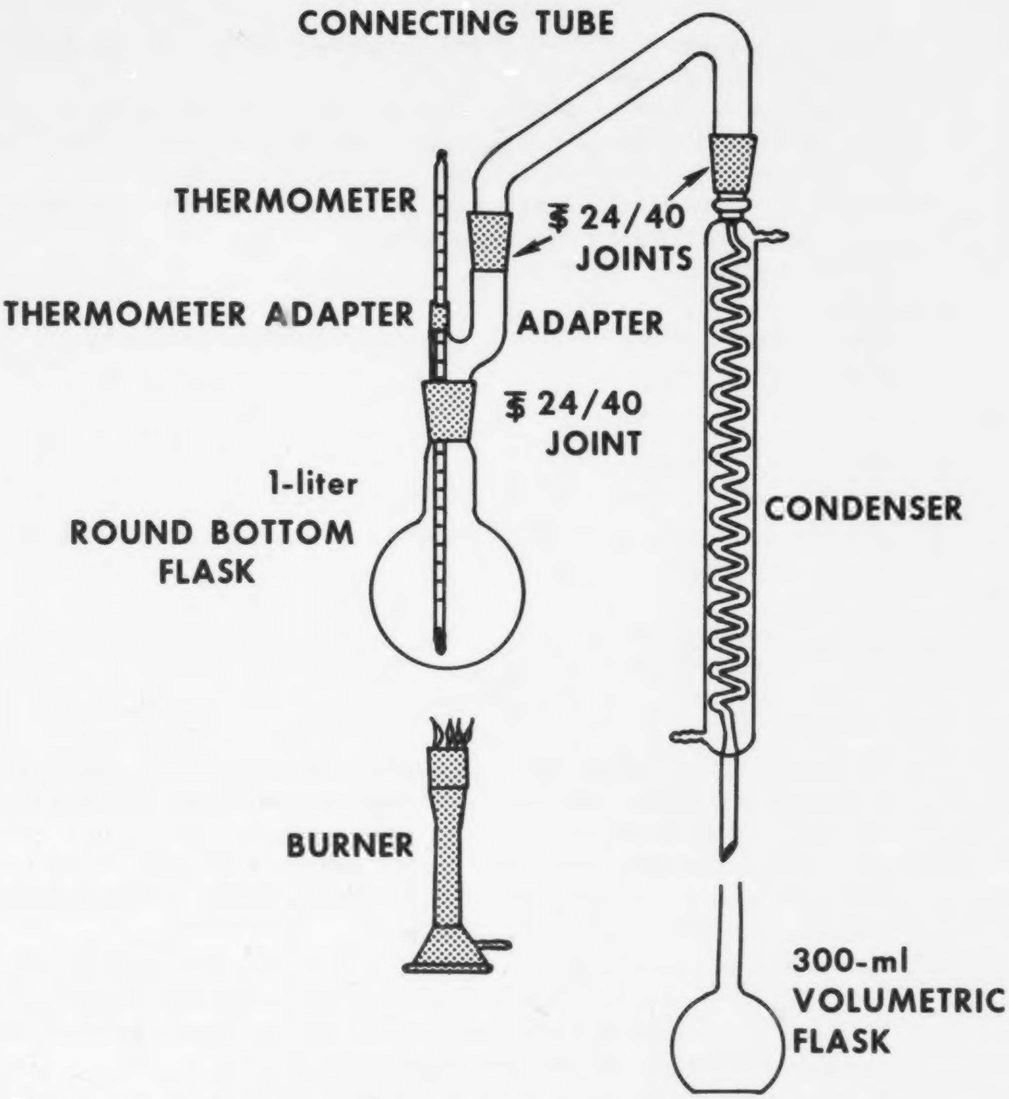
CONNECTING TUBE
THERMOMETER
$ 24/40
JOINTS
THERMOMETER ADAPTER
ADAPTER
$ 24/40
JOINT
1-liter
ROUND BOTTOM
FLASK
CONDENSER
BURNER
300-ml
VOLUMETRIC
FLASK

FIGURE 1 DIRECT DISTILLATION APPARATUS FOR FLUORIDE.

6.2.2 Pipet 5.00 ml each of SPADNS solution (5.5) and zirconyl-acid reagent (5.6) or 10.00 ml of the mixed acid-zirconyl-SPADNS reagent (5.7) to each standard and mix well.

6.2.3 Set photometer to zero with reference solution (5.8) and immediately obtain absorbance readings of standards.

6.2.4 Plot absorbance versus concentration. Prepare a new standard curve whenever fresh reagent is made.

6.2.5 If residual chlorine is present pretreat the sample with 1 drop (0.05 ml) $NaAsO_2$ solution (5.9) per 0.1 mg residual chlorine and mix. Sodium arsenite concentrations of 1300 mg/1 produce an error of 0.1 mg/1 at 1.0 mg/1 F.

6.2.6 Use a 50 ml sample or a portion diluted to 50 ml. Adjust the temperature of the sample to that used for the standard curve.

6.2.7 Perform step 6.2.2 and 6.2.3.

7. Calculations

7.1 Read the concentration in the 50 ml sample using the standard curve (6.2.4)

7.2 Calculate as follows:

$$\text{mg/l F} = \frac{\text{mgF} \times 1{,}000}{\text{ml sample}}$$

7.3 When a sample (ml sample) is diluted to a volume (B) and then a portion (C) is analyzed, use:

$$\text{mg/l F} = \frac{\text{mgF} \times 1{,}000}{\text{ml sample}} \times \frac{B}{C}$$

8. Precision and Accuracy

8.1 On a sample containing 0.83 mg/1 F with no interferences, 53 analysts using the Bellack distillation and the SPADNS reagent obtained a mean of 0.81 mg/1 F with a standard deviation of ±0.089 mg/1.

8.2 On a sample containing 0.57 mg/1 F (with 200 mg/1 SO_4 and 10 mg/1 Al as interferences) 53 analysts using the Bellack distillation obtained a mean of 0.60 mg/1F with a standard deviation of ±0.103 mg/1.

8.3 On a sample containing 0.68 mg/1 F (with 200 mg/1 SO_4, 2 mg/1 Al and 2.5 mg/1 $[Na(PO_3)_6]$ as interferences), 53 analysts using the Bellack distillation obtained a mean of 0.72 mg/1 F with a standard deviation of ±0.092 mg/1. (Analytical Reference Service, Sample 111-B water, Fluoride, August, 1961.)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, p. 389–390 (Method No. 414A, Preliminary Distillation Step) and p. 393–394 (Method 414C SPADNS) 14th Edition, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1179–72, Method A, p. 310 (1976).

FLUORIDE

Method 340.2 (Potentiometric, Ion Selective Electrode)

STORET NO: Total 00951
Dissolved 00950

1. Scope and Application
   1.1 This method is applicable to the measurement of fluoride in drinking, surface and saline waters, domestic and industrial wastes.
   1.2 Concentration of fluoride from 0.1 up to 1000 mg/liter may be measured.
   1.3 For Total or Total Dissolved Fluoride, the Bellack distillation is required for NPDES monitoring but is not required for SDWA monitoring.
2. Summary of Method
   2.1 The fluoride is determined potentiometrically using a fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale or a selective ion meter having a direct concentration scale for fluoride.
   2.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/Ag Cl, Cl^-(0.3), F^-(0.001) LaF/test solution/SCE/.
3. Interferences
   3.1 Extremes of pH interfere; sample pH should be between 5 and 9. Polyvalent cations of Si^{+4}, Fe^{+3} and Al^{+3} interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer (described below) containing a strong chelating agent preferentially complexes aluminum (the most common interference), silicon and iron and eliminates the pH problem.
4. Sampling Handling and Preservation
   4.1 No special requirements.
5. Apparatus
   5.1 Electrometer (pH meter), with expanded mv scale, or a selective ion meter such as the Orion 400 Series.
   5.2 Fluoride Ion Activity Electrode, such as Orion No. 94–09(1).
   5.3 Reference electrode, single junction, sleeve-type, such as Orion No. 90–01, Beckman No. 40454, or Corning No. 476010.
   5.4 Magnetic Mixer, Teflon-coated stirring bar.

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6. Reagents

6.1 Buffer solution, pH 5.0–5.5: To approximately 500 ml of distilled water in a 1 liter beaker add 57 ml of glacial acetic acid, 58 g of sodium chloride and 2 g of CDTA(2). Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer solution to a 1 liter volumetric flask and dilute to the mark with distilled water. For work with brines, additional NaCl should be added to raise the chloride level to twice the highest expected level of chloride in the sample.

6.2 Sodium fluoride, stock solution: 1.0 ml = 0.1 mg F. Dissolve 0.2210 g of sodium fluoride in distilled water and dilute to 1 liter in a volumetric flask. Store in chemical-resistant glass or polyethylene.

6.3 Sodium fluoride, standard solution: 1.0 ml = 0.01 mg F. Dilute 100.0 ml of sodium fluoride stock solution (6.2) to 1000 ml with distilled water.

6.4 Sodium hydroxide, 5N: Dissolve 200 g sodium hydroxide in distilled water, cool and dilute to 1 liter.

7. Calibration

7.1 Prepare a series of standards using the fluoride standard solution (6.3) in the range of 0 to 2.00 mg/1 by diluting appropriate volumes to 50.0 ml. The following series may be used:

Millimeters of Standard (1.0 ml = 0.01 mg/F)	Concentration when Diluted to 50 ml, mg F/liter
0.00	0.00
1.00	0.20
2.00	0.40
3.00	0.60
4.00	0.80
5.00	1.00
6.00	1.20
8.00	1.60
10.00	2.00

7.2 Calibration of Electrometer: Proceed as described in (8.1). Using semilogarithmic graph paper, plot the concentration of fluoride in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale. Calibration of a selective ion meter: Follow the directions of the manufacturer for the operation of the instrument.

8. Procedure

8.1 Place 50.0 ml of sample or standard solution and 50.0 ml of buffer (See Note) in a 150 ml beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 mg/liter F, it may require as long as five minutes to reach a stable meter reading; high concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown using the standard curve. If a selective ion meter is used, read the fluoride level in the unknown sample directly in mg/1 on the fluoride scale.

NOTE: For industrial waste samples, this amount of buffer may not be adequate. Analyst should check pH first. If highly basic (> 9), add 1 N HCl to adjust pH to 8.3.

9. Precision and Accuracy
   - 9.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 0.85 mg/1 fluoride and no interferences was analyzed by 111 analysts; a mean of 0.84 mg/1 with a standard deviation of ±0.03 was obtained.
   - 9.2 On the same study, a synthetic sample containing 0.75 mg/1 fluoride, 2.5 mg/1 polyphosphate and 300 mg/1 alkalinity, was analyzed by the same 111 analysts; a mean of 0.75 mg/1 fluoride with a standard deviation of ±0.036 was obtained.

Bibliography

1. Patent No. 3,431,182 (March 4, 1969).
2. CDTA is the abbreviated designation of 1, 2-cyclohexylene dinitrilo tetraacetic acid, (Matheson, Coleman & Bell, Cat. No. P8661) or cyclohexane diamine tetraacetic acid, (Merck-Titriplex IV or Baker Cat. No. G083).
3. Standard Methods for the Examination of Water and Wastewaters, p 389, Method No. 414A, Preliminary Distillation Step (Bellack), and p 391, Method No. 414B, Electrode Method, 14th Edition (1975).
4. Annual Book of ASTM Standards, Part 31, "Water", Standard D1179–72, Method B, p 312 (1976).

NITROGEN, NITRATE-NITRITE

Method 353.2 (Colorimetric, Automated, Cadmium Reduction)

STORET NO. Total 00630

1. Scope and Application
   1.1 This method pertains to the determination of nitrite singly, or nitrite and nitrate combined in surface and saline waters, and domestic and industrial wastes. The applicable range of this method is 0.05 to 10.0 mg/1 nitrate-nitrite nitrogen. The range may be extended with sample dilution.
2. Summary of Method
   2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N–(1-naphthyl)–ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.
3. Sample Handling and Preservation
   3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml conc. H_2SO_4 per liter) and refrigeration.
   Caution: Samples for reduction column must not be preserved with mercuric chloride.
4. Interferences
   4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered.
   4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.
   4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.
5. Apparatus
   5.1 Technicon AutoAnalyzer (AAI or AAII) consisting of the following components:
      5.1.1 Sampler.
      5.1.2 Manifold (AAI) or analytical cartridge (AAII).
      5.1.3 Proportioning Pump
      5.1.4 Colorimeter equipped with a 15 mm or 50 mm tubular flow cell and 540 nm filters.
      5.1.5 Recorder.

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5.1.6 Digital printer for AAII (Optional).

6. Reagents

6.1 Granulated cadmium: 40–60 mesh (E M Laboratories, Inc., 500 Exec. Blvd., Elmsford, NY 10523, Cat. 2001 Cadmium, Coarse Powder).

6.2 Copper-cadmium: The cadmium granules (new or used) are cleaned with dilute HCl (6.7) and copperized with 2% solution of copper sulfate (6.8) in the following manner:

6.2.1 Wash the cadmium with HCl (6.7) and rinse with distilled water. The color of the cadmium so treated should be silver.

6.2.2 Swirl 10 g cadmium in 100 ml portions of 2% solution of copper sulfate (6.8) for five minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

6.2.3 Wash the cadmium-copper with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.

6.3 Preparation of reduction column AAI: The reduction column is an 8 by 50 mm glass tube with the ends reduced in diameter to permit insertion into the system. Copper-cadmium granules (6.2) are placed in the column between glass wool plugs. The packed reduction column is placed in an up-flow 20° incline to minimize channeling. See Figure 1.

6.4 Preparation of reduction column AAII: The reduction column is a U-shaped, 35 cm length, 2 mm I.D. glass tube (Note 1). Fill the reduction column with distilled water to prevent entrapment of air bubbles during the filling operations. Transfer the copper-cadmium granules (6.2) to the reduction column and place a glass wool plug in each end. To prevent entrapment of air bubbles in the reduction column be sure that all pump tubes are filled with reagents before putting the column into the analytical system.

NOTE 1: A 0.081 I.D. pump tube (purple) can be used in place of the 2 mm glass tube.

6.5 Distilled water: Because of possible contamination, this should be prepared by passage through an ion exchange column comprised of a mixture of both strongly acidic-cation and strongly basic-anion exchange resins. The regeneration of the ion exchange column should be carried out according to the manufacturer's instructions.

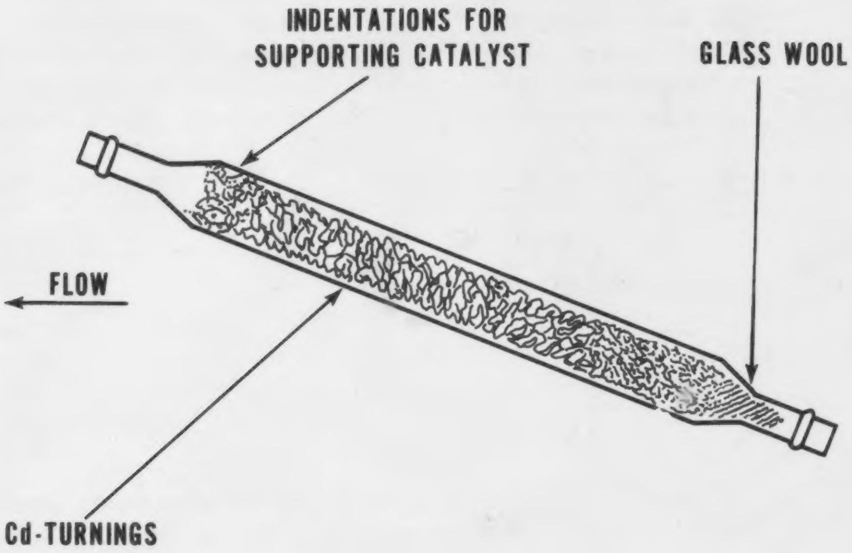
6.6 Color reagent: To approximately 800 ml of distilled water, add, while stirring, 100 ml conc. phosphoric acid, 40 g sulfanilamide, and 2 g N-1-naphthylethylenediamine dihydrochloride. Stir until dissolved and dilute to 1 liter. Store in brown bottle and keep in the dark when not in use. This solution is stable for several months.

6.7 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.

6.8 Copper sulfate solution, 2%: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 ml of distilled water and dilute to 1 liter.

6.9 Wash solution: Use distilled water for unpreserved samples. For samples preserved with H_2SO_4, use 2 ml H_2SO_4 per liter of wash water.

6.10 Ammonium chloride–EDTA solution: Dissolve 85 g of reagent grade ammonium chloride and 0.1 g of disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide and dilute to 1 liter. Add 1/2 ml Brij-35 (available from Technicon Corporation).


INDENTATIONS FOR SUPPORTING CATALYST
GLASS WOOL
FLOW
Cd-TURNINGS

TILT COLUMN TO 20° POSTION

FIGURE 1. COPPER CADMIUM REDUCTION COLUMN
(1 1/2 ACTUAL SIZE)

6.11. Stock nitrate solution: Dissolve 7.218 g KNO_3 and dilute to 1 liter in a volumetric flask with distilled water. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months. 1 ml = 1.0 mg NO_3–N.

6.12 Stock nitrite solution: Dissolve 6.072 g KNO_2 in 500 ml of distilled water and dilute to 1 liter in a volumetric flask. Preserve with 2 ml of chloroform and keep under refrigeration. 1.0 ml = 1.0 mg NO_2–N.

6.13 Standard nitrate solution: Dilute 10.0 ml of stock nitrate solution (6.11) to 1000 ml. 1.0 ml = 0.01 mg NO_3-N. Preserve with 2 ml of chloroform per liter. Solution is stable for 6 months.

6.14 Standard nitrite solution: Dilute 10.0 ml of stock nitrite (6.12) solution to 1000 ml. 1.0 ml = 0.01 mg NO_2-N. Solution is unstable; prepare as required.

6.15 Using standard nitrate solution (6.13), prepare the following standards in 100.0 ml volumetric flasks. At least one nitrite standard should be compared to a nitrate standard at the same concentration to verify the efficiency of the reduction column.

Conc., mgNO_2–N or NO_3-N/l	ml Standard Solution/100 ml
0.0	0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0
2.00	20.0
4.00	40.0
6.00	60.0

NOTE 2: When the samples to be analyzed are saline waters, Substitute Ocean Water (SOW) should be used for preparing the standards; otherwise, distilled water is used. A tabulation of SOW composition follows:

NaCl - 24.53 g/l
$CaCl_2$ - 1.16 g/l
KBr - 0.10 g/l
NaF - 0.003 g/l
$MgCl_2$ - 5.20 g/l
KCl - 0.70 g/l
H_3BO_3 - 0.03 g/l
Na_2SO_4 - 4.09 g/l
$NaHCO_3$ - 0.20 g/l
$SrCl_2$ - 0.03 g/l

7. Procedure

7.1 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH_4OH.

7.2 Set up the manifold as shown in Figure 2 (AAI) or Figure 3 (AAII). Note that reductant column should be in 20° incline position (AAI). Care should be taken not to introduce air into reduction column on the AAII.

7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding distilled water through the sample line.

NOTE 3: Condition column by running 1 mg/l standard for 10 minutes if a new reduction column is being used. Subsequently wash the column with reagents for 20 minutes.

7.4 Place appropriate nitrate and/or nitrite standards in sampler in order of decreasing concentration of nitrogen. Complete loading of sampler tray with unknown samples.

7.5 For the AAI system, sample at a rate of 30/hr, 1:1. For the AAII, use a 40/hr, 4:1 cam and a common wash.

7.6 Switch sample line to sampler and start analysis.

8. Calculations

8.1 Prepare appropriate standard curve or curves derived from processing NO_2 and/or NO_3 standards through manifold. Compute concentration of samples by comparing sample peak heights with standard curve.

9. Precision and Accuracy

9.1 Three laboratories participating in an EPA Method Study, analyzed four natural water samples containing exact increments of inorganic nitrate, with the following results:

Increment as Nitrate Nitrogen mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as Bias, %	Accuracy as Bias, mg N/liter
0.29	0.012	+ 5.75	+0.017
0.35	0.092	+18.10	+0.063
2.31	0.318	+ 4.47	+0.103
2.48	0.176	− 2.69	−0.067

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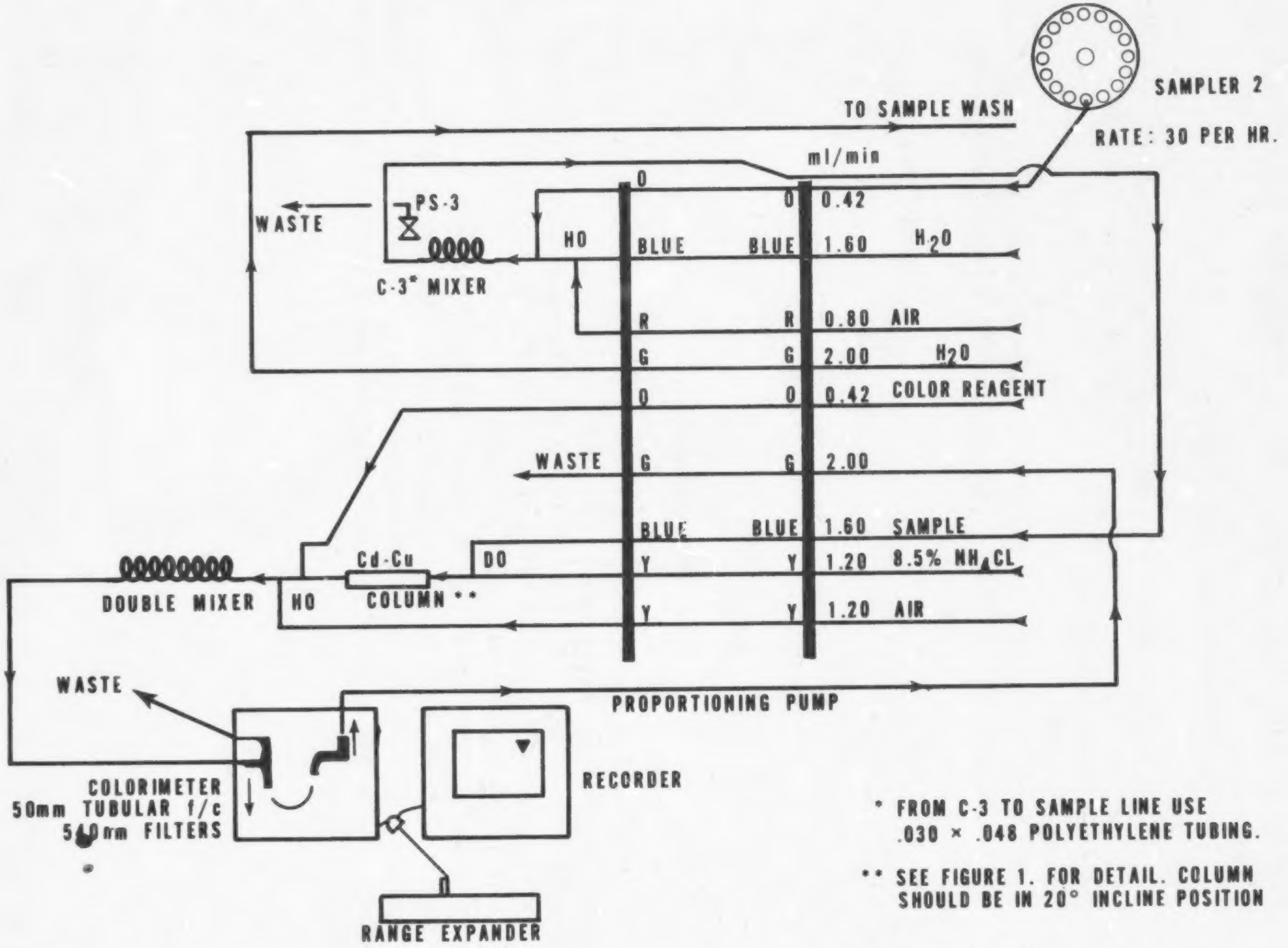
SAMPLER 2
RATE: 30 PER HR.
TO SAMPLE WASH
ml/min
WASTE
PS-3
C-3* MIXER
HO
O
BLUE
R
G
O
G
BLUE
Y
Y
O 0.42
BLUE 1.60 H2O
R 0.80 AIR
G 2.00 H2O
O 0.42 COLOR REAGENT
WASTE
G 2.00
BLUE 1.60 SAMPLE
Y 1.20 8.5% NH4CL
Y 1.20 AIR
DO
Cd-Cu
COLUMN **
HO
DOUBLE MIXER
WASTE
PROPORTIONING PUMP
RECORDER
COLORIMETER
50mm TUBULAR f/c
540nm FILTERS
RANGE EXPANDER

* FROM C-3 TO SAMPLE LINE USE .030 × .048 POLYETHYLENE TUBING.

** SEE FIGURE 1. FOR DETAIL. COLUMN SHOULD BE IN 20° INCLINE POSITION

FIGURE 2. NITRATE - NITRITE MANIFOLD AA-I

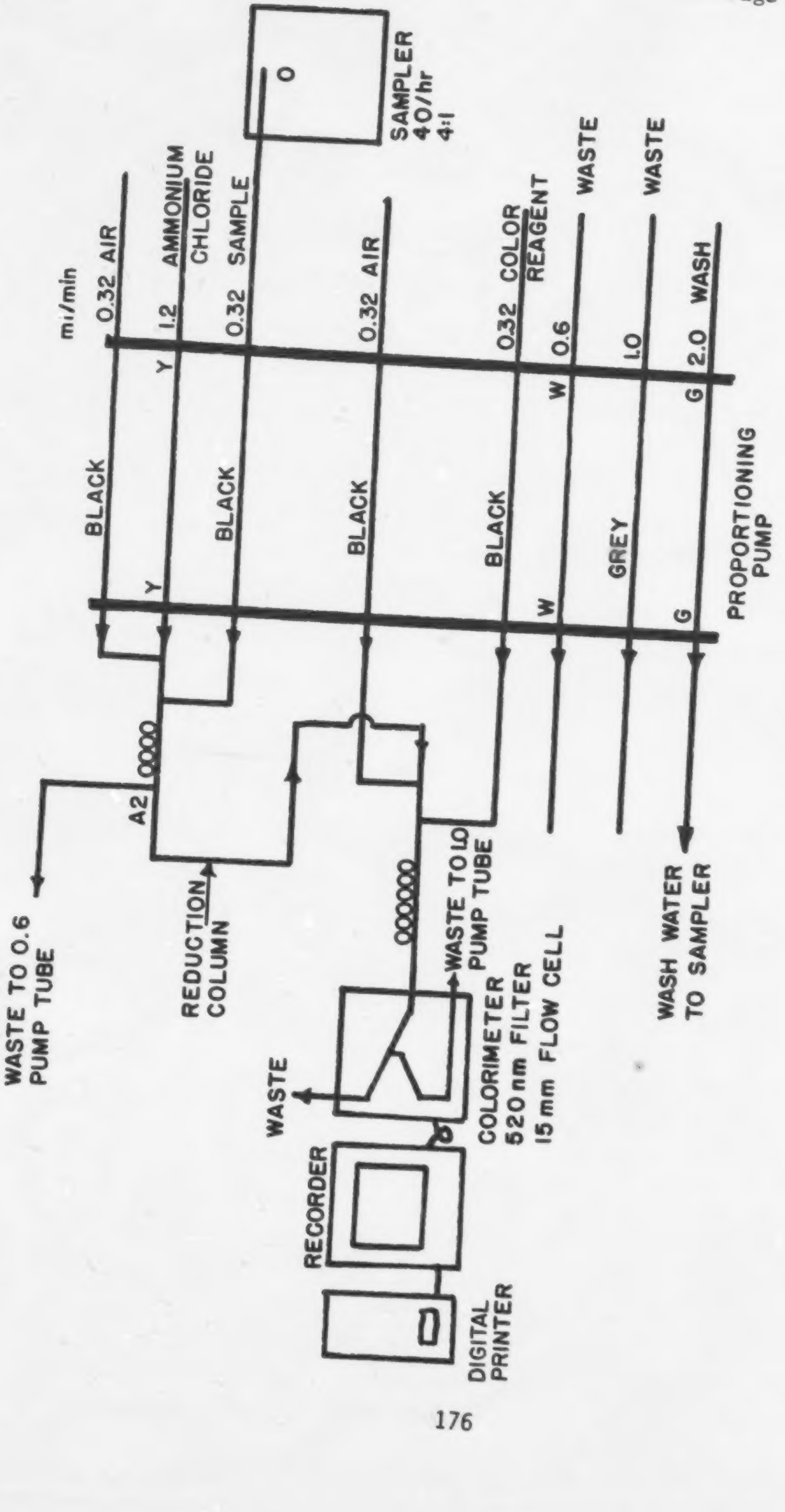
ml/min
0.32 AIR
1.2 AMMONIUM CHLORIDE
0.32 SAMPLE
0.32 AIR
0.32 COLOR REAGENT
0.6 WASTE
1.0 WASTE
2.0 WASH
SAMPLER
40/hr
4:1
O
Y
W
G
BLACK
BLACK
BLACK
BLACK
GREY
Y
W
G
PROPORTIONING PUMP
A2
WASTE TO 0.6 PUMP TUBE
REDUCTION COLUMN
WASTE TO 1.0 PUMP TUBE
WASTE
COLORIMETER
520 nm FILTER
15 mm FLOW CELL
RECORDER
DIGITAL PRINTER
WASH WATER TO SAMPLER

FIGURE 3 NITRATE-NITRITE MANIFOLD AA II

NITROGEN, NITRATE-NITRITE

Method 353.3 (Spectrophotometric, Cadmium Reduction)

STORET NO. Total 00630

1. Scope and Application
    1.1 This method is applicable to the determination of nitrite singly, or nitrite and nitrate combined in drinking, surface and saline waters, domestic and industrial wastes. The applicable range of this method is 0.01 to 1.0 mg/1 nitrate-nitrite nitrogen. The range may be extended with sample dilution.
2. Summary of Method
    2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N–(1-naphthyl)–ethylenediamine dihydrochloride to form a highly colored azo dye which is measured spectrophotometrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.
3. Sample Handling and Preservation
    3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml H_2SO_4 per liter) and refrigeration.
    Caution: Samples for reduction column must not be preserved with mercuric chloride.
4. Interferences
    4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered through a glass fiber filter or a 0.45*u* membrane filter. Highly turbid samples may be pretreated with zinc sulfate before filtration to remove the bulk of particulate matter present in the sample.
    4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.
    4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.
    4.4 This procedure determines both nitrate and nitrite. If only nitrate is desired, a separate determination must be made for nitrite and subsequent corrections made. The nitrite may be determined by the procedure below without the reduction step.

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Issued 1974

5. Apparatus

5.1 Reduction column: The column in Figure I was constructed from a 100 ml pipet by removing the top portion. This column may also be constructed from two pieces of tubing joined end to end. A 10 mm length of 3 cm I.D. tubing is joined to a 25 cm length of 3.5 mm I.D. tubing.

5.2 Spectrophotometer for use at 540 nm, providing a light path of 1 cm or longer.

6. Reagents

6.1 Granulated cadmium: 40–60 mesh (E M Laboratories, Inc., 500 Exec. Blvd., Elmsford, NY 10523, Cat. 2001 Cadmium, Coarse Powder).

6.2 Copper-Cadmium: The cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate in the following manner:

6.2.1 Wash the cadmium with dilute HCl (6.10) and rinse with distilled water. The color of the cadmium should be silver.

6.2.2 Swirl 25 g cadmium in 100 ml portions of a 2% solution of copper sulfate (6.11) for 5 minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

6.2.3 Wash the copper-cadmium with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.

6.3 Preparation of reaction column: Insert a glass wool plug into the bottom of the reduction column and fill with distilled water. Add sufficient copper-cadmium granules to produce a column 18.5 cm in length. Maintain a level of distilled water above the copper-cadmium granules to eliminate entrapment of air. Wash the column with 200 ml of dilute ammonium chloride solution (6.5). The column is then activated by passing through the column 100 ml of a solution composed of 25 ml of a 1.0 mg/1 NO_3–N standard and 75 ml of ammonium chloride – EDTA solution (6.4). Use a flow rate between 7 and 10 ml per minute.

6.4 Ammonium chloride – EDTA solution: Dissolve 13 g ammonium chloride and 1.7 g disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide (6.9) and dilute to 1 liter.

6.5 Dilute ammonium chloride-EDTA solution: Dilute 300 ml of ammonium chloride-EDTA solution (6.4) to 500 ml with distilled water.

6.6 Color reagent: Dissolve 10 g sulfanilamide and 1 g N(1-naphthyl)–ethylene-diamine dihydrochloride in a mixture of 100 ml conc. phosphoric acid and 800 ml of distilled water and dilute to 1 liter with distilled water.

6.7 Zinc sulfate solution: Dissolve 100 g $ZnSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 liter.

6.8 Sodium hydroxide solution, 6N: Dissolve 240 g NaOH in 500 ml distilled water, cool and dilute to 1 liter.

6.9 Ammonium hydroxide, conc.

6.10 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.

6.11 Copper sulfate solution, 2%: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 ml of distilled water and dilute to 1 liter.

6.12 Stock nitrate solution: Dissolve 7.218 g KNO_3 in distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform per liter. This solution is stable for at least 6 months. 1.0 ml = 1.00 mg NO_3–N.

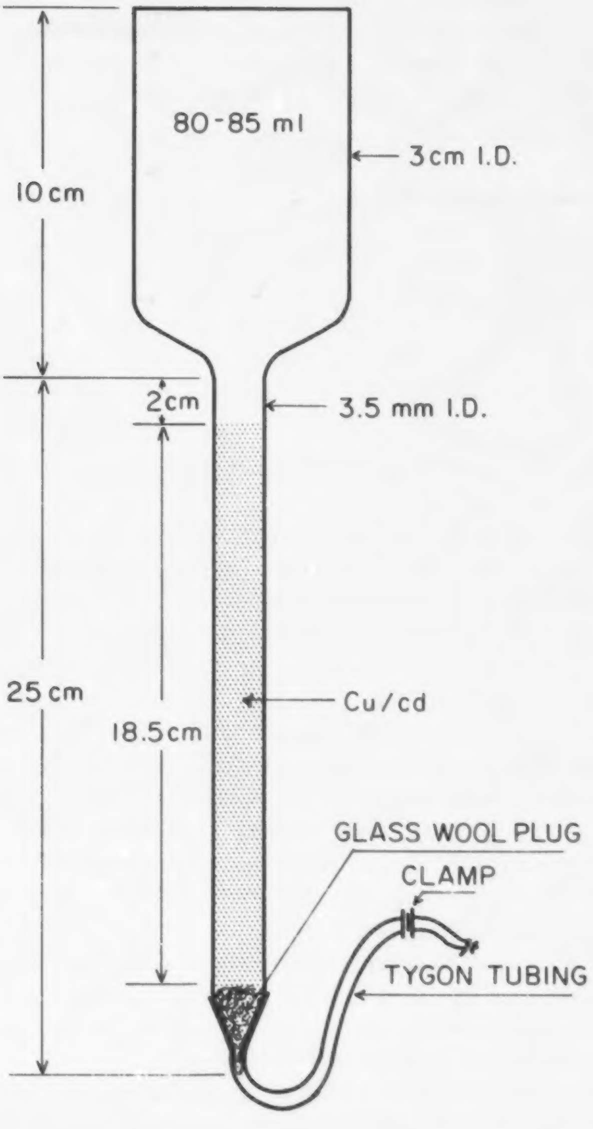
80-85 ml
3cm I.D.
10 cm
2cm
3.5 mm I.D.
25 cm
18.5cm
Cu/cd
GLASS WOOL PLUG
CLAMP
TYGON TUBING

FIGURE 1. REDUCTION COLUMN

6.13 Standard nitrate solution: Dilute 10.0 ml of nitrate stock solution (6.12) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO_3–N.

6.14 Stock nitrite solution: Dissolve 6.072 g KNO_2 in 500 ml of distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform and keep under refrigeration. Stable for approximately 3 months. 1.0 ml = 1.00 mg NO_2–N.

6.15 Standard nitrite solution: Dilute 10.0 ml of stock nitrite solution (6.14) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO_2–N.

6.16 Using standard nitrate solution (6.13) prepare the following standards in 100 ml volumetric flasks:

Conc., mg-NO_3–N/l	ml of Standard Solution/100.0 ml
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0

7. Procedure

7.1 Turbidity removal: One of the following methods may be used to remove suspended matter.

7.1.1 Filter sample through a glass fiber filter or a 0.45*u* membrane filter.

7.1.2 Add 1 ml zinc sulfate solution (6.7) to 100 ml of sample and mix thoroughly. Add 0.4–0.5 ml sodium hydroxide solution (6.8) to obtain a pH of 10.5 as determined with a pH meter. Let the treated sample stand a few minutes to allow the heavy flocculent precipitate to settle. Clarify by filtering through a glass fiber filter or a 0.45*u* membrane filter.

7.2 Oil and grease removal: Adjust the pH of 100 ml of filtered sample to 2 by addition of conc. HCl. Extract the oil and grease from the aqueous solution with two 25 ml portions of a non-polar solvent (Freon, chloroform or equivalent).

7.3 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH_4OH. This is done to insure a sample pH of 8.5 after step 7.4.

7.4 To 25.0 ml of sample or an aliquot diluted to 25.0 ml, add 75 ml of ammonium chloride-EDTA solution (6.4) and mix.

7.5 Pour sample into column and collect sample at a rate of 7–10 ml per minute.

7.6 Discard the first 25 ml, collect the rest of the sample (approximately 70 ml) in the original sample flask. Reduced samples should not be allowed to stand longer than 15 minutes before addition of color reagent, step 7.7.

7.7 Add 2.0 ml of color reagent (6.6) to 50.0 ml of sample. Allow 10 minutes for color development. Within 2 hours measure the absorbance at 540 nm against a reagent blank. **NOTE:** If the concentration of sample exceeds 1.0 mg NO_3–N/1, the remainder of the reduced sample may be used to make an appropriate dilution before proceeding with step 7.7.

7.8 Standards: Carry out the reduction of standards exactly as described for the samples. At least one nitrite standard should be compared to a reduced nitrate standard at the same concentration to verify the efficiency of the reduction column.

8. Calculation

8.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against NO_3–N mg/1. Compute concentration of samples by comparing sample absorbance with standard curve.

8.2 If less than 25 ml of sample is used for the analysis the following equation should be used:

$$\mathrm{mgNO_2} + \mathrm{NO_3} - \mathrm{N/l} = \frac{A \times 25}{\text{ml sample used}}$$

where:

A = Concentration of nitrate from standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using sewage samples at concentrations of 0.04, 0.24, 0.55 and 1.04 mg NO_3 + NO_2-N/1, the standard deviations were ±0.005, ±0.004, ±0.005 and ±0.01, respectively.

9.2 In a single laboratory (EMSL), using sewage samples at concentrations of 0.24, 0.55, and 1.05 mg NO_3 + NO_2–N/1, the recoveries were 100%, 102% and 100%, respectively.

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2.6.2 Quality Control Procedures

Instrument calibration is included in the analytical procedures for fluoride and nitrate. Discussion of method blanks, replicate analyses, and laboratory control standards follows, with each activity, its frequency, control limits, and corrective action summarized in Table 2-9.

A. Sample Spiking

For fluoride and nitrate analyses, the first 10 samples from each type (drinking water, sump water, surface water, and ground water) must be spiked at the concentration level shown below. If recoveries for these spikes are between 85 and 115 percent, then one of each of the next 20 samples of each type must be spiked. The measured recoveries of these additional spikes must also fall within 85 to 115 percent. If the percent recoveries are not within these limits, the method of standard additions must be used for analyses on all samples of that type.

Anion	Spike concentration* (mg/l)
Fluoride	1.0
Nitrate	10.0

B. Method Blanks

For all methods, one method blank (reagent water) must be processed through the entire laboratory analytical procedure for each set of samples processed in a group at the same time on the same day. Normally, this will be one method blank for every 5 to 15 samples, depending on how many samples are in a given batch. If laboratory contamination is found in the method blanks and it is judged that the same contaminants are present in the environmental samples, reported values for these analytes must be reduced by the amount found in the blank.

C. Replicate Analyses

For all methods, intralaboratory precision of the environmental measurements must be evaluated by the measurement of one duplicate of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These data must be reported with the laboratory results and will be used by EPA in assessing the overall precision of the data.

D. Laboratory Control Standards

For all methods, laboratory control standards (LCS) shall be employed to control systematic method and operator errors. The LCS is a solution of one

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*Spike levels are prior to concentrating.

TABLE 2-9. INTERNAL QC REQUIREMENTS — ANIONS IN WATER

Operation check	Frequency	Control limits	Corrective action planned
Method blank (reagent water)	One per analysis batch[a]/ analysis day	No significant concentrations found	Correct for blank Check analytical procedure
Laboratory control standard (LCS)	One per analysis batch[a]/ analysis day	As specified in text	Check analytical procedure Analyze second reference sample
Spiked samples (initial study)	First 10 of each type of water sample	85-115% recovery of each anion	Use standard additions
Spiked samples (check)	If control limits of above are met, one of the next 20 water samples of each type.	85-115% recovery of each anion	Use standard additions
Replicate analysis	One of every 20 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

[a] Analysis batch = group of samples processed as a set, usually containing 15 samples or less.

or more analytes of known concentration in reagent water. Separate LCSs will be used for each method, and each will be prepared using either EMSL-Cincinnati quality control concentrates or standards supplied by the individual laboratory. One LCS must be processed through the entire analytical method for each set of samples processed in a group at the same time on the same day. Normally, this will be one LCS for every 5 to 15 samples, depending on how many samples are processed in a given batch. A control chart should be maintained; the control limits to be used, expressed as a percentage of the true value, and the required concentration ranges for fluoride and nitrate are shown below.

Analyte	Control limits
Method 340.1 or 340.2	
Fluoride (0.5-1.5 mg/l)	92-108%
Method 353.2 or 353.3	
Nitrate (2-10 mg/l)	92-108%

All measurements of LCS analytes must be expressed in terms of the percentage of true values, and these must be compared with the control limits. Any value that falls beyond the control limits shall trigger an investigation to determine the cause of the deviation and a correction of the problem. Values of environmental measurements from samples processed during that same work shift must be remeasured or not reported unless a satisfactory justification is prepared.

2.7 TOTAL ORGANIC CARBON(TOC)

2.7.1 Analytical Procedures

The procedures described in Method 415.1 from "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, are to be used for the measurement of total organic carbon (TOC) in water samples. A copy of this procedure is included in this section.

Preservation of samples for TOC analysis (other than refrigeration at 4°C) is performed in the laboratory rather than in the field. Chemical preservation consists of adjusting the sample pH to less than 2 using HCl or H_2SO_4 if analysis cannot be performed within two (2) hours of collection. Note that this preserved aliquot is separated from that to be used for analysis of TOX (Section 2.8 of this Appendix).

STORET NO. Total 00680
Dissolved 00681

1. Scope and Application
   1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
   1.2 The method is most applicable to measurement of organic carbon above 1 mg/1.
2. Summary of Method
   2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.
3. Definitions
   3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
      A) soluble, nonvolatile organic carbon; for instance, natural sugars.
      B) soluble, volatile organic carbon; for instance, mercaptans.
      C) insoluble, partially volatile carbon; for instance, oils.
      D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
      E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
   3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

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4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples. **NOTE 1:** A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified ($pH \leq 2$) with HCl or H_2SO_4.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior.

7. Reagents

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.

NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as Bias, %	Accuracy as Bias, mg/liter
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574–79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

2.7.2 Quality Control Procedures

Quality control procedures required for the analysis of total organic carbon in water samples are described below. The QC activities, their frequency, control limits and corrective action are summarized in Table 2-10.

A. Method Blanks

One method blank (reagent water) must be processed through the entire analytical procedure for each set of samples to be analyzed in a given 8 hour work shift. The method blank must not contain levels of TOC. If common laboratory contamination is found in the method blanks, reported values for TOC in environmental samples must be reduced by the amount found in the blanks.

B. Replicate Analyses

Intralaboratory precision of the environmental measurements will be evaluated by one duplicate (split) of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These results must be reported as part of the data base on the Love Canal Study.

TABLE 2-10. INTERNAL QC REQUIREMENTS - TOTAL ORGANIC CARBON

Operation check	Frequency	Control limits	Corrective action planned
Method blank (reagent water)	Daily before start of analysis and after every 8 hours of analysis	No significant concentrations found	Check analytical procedure
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

2.8 TOTAL ORGANIC HALOGENS (TOX)

2.8.1 Analytical Procedures

The method for the determination of total organic halogens (TOX) in water utilizes the Dohrmann DX-20 TOX Analyzer system, which is comprised of two functionally independent units; an adsorption module (AD-2), and a microcoulometric analyzer (MC-1). Adsorption of organics from water onto granular activated carbon (GAC) packed in microcolumns and subsequent desorption of inorganic halides by washing the GAC with nitrate solution is performed using the AD-2 module. Combustion of sorbed organics along with the GAC and immediate microcoulometric silver ion titration of the halides produced is performed with the MC-1 module.

The analyzer is standardized using an organic halide such as 2,4,6-trichlorophenol. The halide concentration found is calculated and reported as percent of the known concentration recovered. Sample results are corrected for the percent recovery acheived on a standard close to the concentration of the sample. It should be noted that recoveries may vary at different concentration levels and that the standard should be freshly prepared when recovery is low.

The detection limit of this method under ideal conditions is 1 µg/l of organic halides. Organic halides are defined as all organic species containing chlorine, bromine, and iodine. Fluorine containing species are not determined by this method.

Preservation of samples for TOX consists of maintaining the temperature at 4°C. Note that TOX aliquots must be separated from TOC aliquots prior to acidification of the latter sample.

The procedure for both standards and samples consists of the following steps:

A. Adsorption--Wash Step

In the adsorption--wash step, 0.1 M sodium sulfite solution is added to the water sample (1 ml sodium sulfite per 0.5 liter of sample) to reduce residual chlorine in the water to chloride. To the same sample, reagent grade nitric acid is added to acidify the sample to about pH 2. One of the four sample channel reservoirs of the AD-2 module is filled to capacity (130 ml) with the pretreated sample.

The granular activated carbon (GAC) for adsorption of the TOX from the water sample is contained in glass microcolumns (2 mm ID x 6 mm OD x 50 mm). Two glass columns, each packed with about 40 mg of 100/120 mesh GAC, are connected in series with the sample reservoir containing the pretreated sample. Where samples are known to be low in TOX or are highly diluted, analyzing of the second column packing is omitted. Typically, only the first column is analyzed and past experience is used as a guideline to determine if it is necessary to analyze the second column.

The sample reservoir is pressurized to 30 psi with nitrogen, causing the water sample to be forced through the connected GAC-packed columns at a rate of about 3 ml/min. Typically 25 to 100 ml of water sample pass through the GAC columns. Column effluent is measured by means of an appropriate size volumetric flask placed below the reservoir.

When the adsorption step is completed, the GAC columns, still connected in series, are removed from the sample channel and connected in series below the nitrate wash channel reservoir. The nitrate reagent rinse is needed to wash out and desorb inorganic halide ions from the adsorption columns. Two ml of a 5,000 ppm nitrate solution as potassium nitrate is passed through the columns.

The sample columns are disconnected from the adsorption module and removed from their housings when the nitrate wash step is completed. The GAC columns are now ready for the combustion-determination step. The used sample reservoir is rinsed twice with reagent water and can be used for adsorption of the next sample.

B. Combustion--Determination Step

The MC-1 microcoulometric analyzer module provides the means for measuring the TOX content of GAC after adsorption of organics contained in the water sample. The GAC is removed from its column and deposited directly into a quartz sample boat residing in a CO_2 environment in the analyzer inlet tube. The inlet tube is sealed, and when the reference baseline value has stabilized, the "start" switch is activated.

A magnetically coupled mechanism advances the boat into a 250°C vaporization zone which is swept with pure CO_2. In this atmosphere, the entrained water and volatile organics in the GAC are vaporized. The volatilized organic halides are carried through an 800°C zone where organics are oxidized and halides are converted to HX. The gases then flow into a halogen specific coulometric titration cell. The cell consists of two pairs of electrodes: a generator pair which generates the silver ion titrating agent, and a sensor/reference pair which monitors the concentration of the titrant in the cell. As the halides enter the cell, silver halide precipitates and reduces the silver titrant ion concentration. The generating current needed to restore the cell to its original titrant concentration is integrated and displayed digitally as micrograms of chlorine.

Two minutes after "start," the boat with the GAC is advanced in the pyrolysis tube from the vaporization zone into the 800°C oxidation zone. Simultaneously, gas switching occurs changing the boat environment into a 100 percent O_2 stream. Under these conditions, all carbonaceous material, including the GAC, in the boat is oxidized. The halogens released during this phase are also converted to their corresponding HX. The HX is titrated as before, and the digital display indicates the total halide content of the GAC column.

After 10 minutes the boat is automatically retracted to its loading position for cooling and the analyzer is ready to accept the next sample.

C. Calculation

Total halide concentration of the sample or standard is calculated as follows:

1. When two columns are analyzed

$$\text{TOX } (\mu\text{g Cl/liter}) = (C_1 + C_2 - 2C_3)\,\frac{1000}{V}$$

2. When one column is analyzed

$$\text{TOX } (\mu\text{g Cl/liter}) = (C_1 - C_3)\,\frac{1000}{V}$$

where,

C_1 = halide content of 1st (upper) GAC column (µg Cl);

C_2 = halide content of 2nd (lower) GAC column (µg Cl);

C_3 = halide content of blank GAC column washed with 2 ml nitrate solution

V = volume of sample processed (ml)

The TOX blank (C_3) from the GAC is determined daily; a typical blank from 40 mg of washed GAC should be $\leq$ 1.0 µg as chlorine.

3. The percent recovered of the known concentration in the standard is calculated. Known standards are usually run before, after and during each day's run at concentration levels close to that of the samples analyzed. The average percent recovery of these standards is used to correct sample results as follows:

$$\text{Reported Sample TOX Value} = \frac{\text{TOX in sample } (\mu\text{g Cl/liter})}{\text{Average percent recovery of standard}}$$

2.8.2 Quality Control Procedures

Quality control procedures required for the analysis of total organic halide in water samples are described below. The QC activities, their frequency, control limits and corrective action are summarized in Table 2-11.

A. Method Blanks

One method blank (reagent water) must be processed through the entire analytical procedure for each set of samples to be analyzed in a given 8-hour work shift. The method blank must not contain levels of TOX. If common laboratory contamination is found in the method blanks, reported values for TOX in environmental samples must be reduced by the amount found in the blanks.

B. Replicate Analyses

Intralaboratory precision of the environmental measurements will be evaluated by one duplicate (split) of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These results must be reported as part of the data base on the Love Canal Study.

2.9 DIOXINS (Tetrachlorodibenzo-p-dioxins)

2.9.1 Analytical Procedures

Water samples are vigorously shaken and an aliquot extracted with organic solvent. The organic extract is then subjected to various washing and liquid chromatographic procedures to remove organic interferences and the dioxins (TCDDs) present in the extract determined by gas chromatography-mass spectrometry. 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is used as a standard for quantifying samples and $^{37}Cl_4$-2,3,7,8-TCDD is used as an internal standard.

This section contains the extraction and washing procedures specific to water samples; the extract produced is then handled as directed in Section 7.6 of this appendix. Quality Control procedures for water samples are given in Section 2.9.2.

A. Sample Handling and Preservation

TCDD is toxic and can pose grave health hazards if handled improperly. Techniques used for handling radioactive and infectious material are applicable and only qualified individuals trained in laboratory procedures and familiar with the hazards of TCDD should handle this substance. Females of childbearing age should not work with this material.

Water samples are shipped to the laboratory under chain-of-custody procedures and internal chain of custody must be maintained. All water samples should have been preserved in the field by adjusting the pH to 6-8. 10 N NaOH or $1:1H_2SO_4$ is used, if necessary, and the amount added noted on the analysis tag. All water samples are maintained at 4°C until analysis.

B. Reagents

- Potassium hydroxide, anhydrous sodium sulfate, and sulfuric acid, ACS Reagent Grade,
- Methanol, hexane, methylene chloride and benzene, "Distilled in Glass" quality,
- Petroleum ether (low boiling), Omnisone Quality from Matheson, Coleman, and Bell, or equivalent,
- WOEIM basic alumina, Activity Grade 1,
- Prepurified nitrogen gas,
- Double-distilled water

- Dioxin standards can be obtained from the sources listed below:

$^{37}\mathrm{Cl}_4$-2,3,7,8-TCDD-KOR Isotopes, Cambridge, Mass.
1,2,3,4-TCDD-Analabs, Inc., North Haven, Connecticut
2,3,7,8-TCDD-Dow Chemical Co., Midland, Michigan

1,3,6,8 1,3,7,9 1,4,6,9 1,3,7,8 1,2,6,8 1,2,7,9 1,2,6,9 1,2,7,8 1,2,6,7 1,2,8,9	H.R. Buser Swiss Federal Research Station Ch-820 Wadenswil, Switzerland

C. Sample Extraction/Cleanup Procedures

1. Manually shake the amber bottle containing the water sample, quickly withdraw a 40 ml aliquot and place in a 125 ml flint glass bottle (equipped with Teflon-lined screw cap).

2. Spike the 40 ml aliquot by addition of 25 ng of $^{37}\mathrm{Cl}_4$-2,3,7,8-TCDD (25 µl of benzene solution containing 1 ng $^{37}\mathrm{Cl}_4$-2,3,7,8-TCDD per µl) and shake for 1 minute.

3. Add to the spiked aqueous sample 40 ml of petroleum ether and extract the sample by shaking for 20 minutes using a Burrell Wrist Action shaker.

4. Discard the aqueous layer.

5. Extract the organic solution with 50 ml of 20 percent (w/v) potassium hydroxide by shaking for 10 minutes. Allow for complete separation and remove aqueous base (bottom) layer to base waste bottle.

6. Extract the organic solution with 50 ml of doubly distilled water by shaking the sample for 2 minutes. Allow time for complete layer separation and discard the aqueous (bottom) layer.

7. Extract the organic solution with 50 ml of concentrated sulfuric acid (cautiously adding sulfuric acid) by shaking the sample for 15 minutes. Allow for complete layer separation and discard acid (bottom) layer into acid waste bottle.

8. Repeat Step 7 until acid layer is nearly transparent.

9. Extract the organic solution with 50 ml of doubly distilled water by shaking for 2 minutes. Allow for complete separation and remove aqueous (bottom) layer.

10. Dry the organic layer over sodium sulfate and then quantitatively transfer a portion of the organic layer to a clean test tube and reduce the volume to incipient dryness using a stream of prepurified nitrogen and while maintaining the test tube in a 55° water bath.

The dried extract should now be further cleaned up using the procedure given in Section 7.6 of this Appendix. This section also contains GC/MS analysis specifications, analytical criteria for positive TCDD results and reference material.

D. Reporting of Analytical Results

Analytical results must satisfy specific analytical criteria to be considered positive results. The criteria used by the EPA Health Effects Research Laboratory (HERL)/RTP for TCDD are given in Section 7.6 of this appendix. Only analytical results meeting these or comparable criteria should be reported. All positive results on collected samples will be confirmed by the EPA referee laboratory, HERL/RTP.

The analytical results reported for each sample should include: sample identification, percent recovery for TCDD, minimum limits of detection for TCDDs (ng/ml), TCDDs detected (ng/ml), and comments pertaining to each analysis as necessary.

2.9.2 Quality Control Procedures

Quality control procedures to be utilized in the analysis of TCDD are described below in some detail. In addition, the QC activities and the type, frequency, control limits and corrective action for each are summarized in Table 2-12.

A. Calibration and Standardization

A calibration curve is prepared by analyzing a series of standard solutions containing varying concentrations of 2,3,7,8-TCDD; each standard solution contains the same concentration of $^{37}Cl_4$-2,3,7,8-TCDD. The ratio of the areas of the peaks which are indicative of 2,3,7,8-TCDD and $^{37}Cl_4$-2,3,7,8-TCDD is plotted as a function of the concentration of 2,3,7,8-TCDD. Use of the internal standard technique automatically corrects the results for any losses of TCDD incurred during sample processing.

B. Calibration Check Standards/Standard Validation

Primary quantification standards containing both 2,3,7,8-TCDD and $^{37}Cl_4$-2,3,7,8-TCDD are prepared by EPA, HERL/RTP and submitted to the analytical laboratory by the Prime Contractor for use in validating the laboratory's TCDD standards.

C. Control Samples/Method Validation

Prior to actual analysis, the methodology which has been developed is tested and optimized by analyzing a series of control samples - reagent water to which known quantities of TCDD have been added. Generally, for samples such as those analyzed in this project, the method is deemed acceptable if 70-100 percent of the added TCDD is recovered and detected in the analysis. If this is not the case, then modifications are made to the method to further optimize the performance, and additional spiked samples are analyzed using the revised procedures. This is repeated until a satisfactory level of performance is obtained for the spiked samples.

D. Laboratory Control Standards (LCS)

Reagent water spiked with TCDD is used as a laboratory control standard (LCS) to identify any systematic method or operator errors. If the recovery for the LCS is not within the acceptance limits identified during the method validation, then an entire new series of LCS analyses is repeated, and the methodology is thoroughly checked to determine the source of error. Selected Love Canal samples analyzed during any period when unacceptable QC data are obtained are also reanalyzed to ensure that these were not affected by any temporary aberrations in the methods or procedures.

TABLE 2-12. INTERNAL QC REQUIREMENTS--DIOXINS IN WATER

Operation check	Frequency	Control limits	Corrective action planned
Calibration of instrument	Daily before analysis of samples	Not applicable	Not applicable
Internal standard	Added to every sample and standard	To be determined	Report percent recovery Check analytical procedure
Calibration check	One per analysis batch[a]	To be determined	Check analytical procedure Analyze second reference standard Invalidate results and generate fresh standard curve
Method Validation	Before use of new sample cleanup/analysis procedures	To be determined	Modify cleanup or analysis procedure
Laboratory control standard (LCS)	One per analysis batch[a]	As determined in Method validation	Check analytical procedure Analyze second reference sample Invalidate results
Method blank	One per analysis batch[a]	No significant concentrations found	Correct for blank Check analytical procedure
Analytical criteria	Each positive TCDD result	As in Section 7.6, or equivalent	Report TCDD not detected

[a] Analysis batch = group of samples processes as a set, usually containing 15 samples or less.

E. Method Blanks

One method blank (reagent water) shall be carried through the sample preparation and analysis procedures to ensure that sample results can be corrected for compounds contributed by the reagents and chemicals used in the procedures.

F. Analytical Criteria/Confirmation of Positive Results

All positive TCDD results are tested by the criteria given in Section 7.6 or equivalent criteria, before reporting. The extracts of samples in which native TCDDs have been found are sent to the EPA referee laboratory, HERL/RTP for confirmatory analyses.

2.10 RADIOACTIVITY

2.10.1 Analytical Procedures

The water samples are collected in 300-ml teflon-lined aluminum cans. No preservatives are added; the cans are sealed, and shipped to the analytical laboratory.

The analysis for gamma-emitting radionuclides is performed by solid-state high resolution gamma detectors (lithium drifted germanium or intrinsic germanium detectors) connected to a tri-computer based gamma-ray spectrometer for on-line spectral acquisition and resolution.

The tritium analysis of these water samples is performed by distilling an aliquot of the sample, mixing a portion of the distillate with liquid scintillation solution, and analyzing with a liquid scintillation counter.

For other radionuclides, the radionuclides are separated from the sample by either wet-chemical, ion-exchange, or other appropriate methods and then analyzed by alpha-spectrometry or proportional beta counting, depending on the radionuclide of concern. Procedures for these measurements are not included in this Appendix.

A. Gamma-Ray Spectral Analysis

The sample, sealed in the aluminum can, is placed in a polyethylene bag and centered on the endcap of the detector for analysis. Each gamma-ray spectrum consists of 4096 channels calibrated at approximately 1/2 kev per channel. The minimum detectable concentration (MDC) for a given radionuclide is dependent on the abundance of the gamma-rays being emitted and their energy. For cesium-137 the MDC is approximately 50 picocuries/liter (pCi/ℓ) in water samples.

B. Tritium Analysis

Azeotopic distillation is used to remove contaminants in water samples. A 5-ml portion of the distillate is pipetted into a polyethylene counting vial and 20-ml of liquid scintillation solution is added to the vial. The vial is then analyzed by liquid scintillation counting. The MDC for tritium in water is approximately 300 to 400 pCi/ℓ.

2.10.2 Quality Control Procedures

Quality control procedures applicable to gamma-ray spectrometry and tritium analyses are described below. The quality control procedures and their frequencies are summarized in Table 2-13.

A. Calibration Standard

All radionuclide standards used in the gamma-ray spectrometry and tritium analyses are traceable to NBS. The standards are prepared and placed in the appropriate geometry by the Quality Assurance Division of the Environmental Monitoring Systems Laboratory-Las Vegas.

B. Backgrounds

For gamma-ray spectral analysis background spectra are acquired once each week. For a tritium background sample a deep well water (tritium free) sample undergoes azeotopic distillation, preparation, and liquid scintillation counting identical to a routine sample. Each batch of samples analyzed by liquid scintillation counting contains one background sample.

C. Replicate Analysis

Intralaboratory precision of the environmental measurements will be evaluated from the results of duplicate measurements on one of every 10 environmental samples. The duplicate for gamma-ray measurement is the original sample; for tritium, the duplicate is a second aliquot of the sample carried through the preparation and measurement procedures.

D. Control Charts

Control charts are maintained for gamma-ray spectrometry. Plotted are background, standard's activity, efficiency, and full width of the photopeak at 1/2 maximum height. Control charts for the liquid scintillation counters contain plots of the background and standard's activity in counts per minute.

TABLE 2-13. INTERNAL QC REQUIREMENTS - RADIOACTIVITY IN WATER

Analysis	Operation check	Frequency	Control limits	Planned corrective action
Gamma	Background	Weekly	±3 standard deviations	Clean detector Check procedures Check data Possibly recalculate results
	Energy calibration	Daily before start of analyses	Subjective	Recalibrate Check procedures Check electronics Check previous day's data
	Efficiency calibration	As needed		Analyze standard Possibly reanalyze samples Recalibrate
	Participation in cross check programs	Bi-monthly, quarterly	±3 standard deviations	Check procedures Recalibrate
	Replicate analysis	One of every 10 samples	±3 standard deviations	Check procedures Analyze standard Possibly reanalyze samples
Tritium	Background	Each run	±3 standard deviations	Check scintillation solution Check procedures Reanalyze background Clean counters Check data Possibly reclaculate results or reanalyze samples
	Analyze standard	Each run	±3 standard deviations	Reanalyze standard Check procedure Check standard Reanalyze samples
	Replicate analysis	One of every 10 samples	±3 standard deviations	Check procedures Analyze standard Possibly reanalyze samples

2.11 pH

2.11.1 Analytical Procedures

Groundwater samples are analyzed for pH using the procedures specified in Method 150.1 in "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, which is reproduced in this section.

Samples are to be analyzed as soon as possible after receipt from the Sample Bank, but definitely within 6 hours. Sample preservation consists of refrigeration at 4°C until analysis, at which time samples are allowed to warm to room temperature. Precautions regarding sample temperature at the time of measurement are given in Section 8.3 of Method 150.1.

pH

Method 150.1 (Electrometric)

STORET NO.
Determined on site 00400
Laboratory 00403

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
   2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.
3. Sample Handling and Preservation
   3.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.
   3.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.
4. Interferences
   4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
   4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.
   4.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1 + 9) may be necessary to remove any remaining film.
   4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.
5. Apparatus
   5.1 pH Meter-laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

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5.2 Glass electrode.

5.3 Reference electrode–a calomel, silver-silver chloride or other reference electrode of constant potential may be used.

NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel type filling materials that require minimal maintenance.

5.4 Magnetic stirrer and Teflon-coated stirring bar.

5.5 Thermometer or temperature sensor for automatic compensation.

6. Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is necessary.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.

7. Calibration

7.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart.

7.2.1 Various instrument designs may involve use of a "balance" or "standardize" dial and/or a slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until readings are within 0.05 pH units of the buffer solution value.

8. Procedure

8.1 Standardize the meter and electrode system as outlined in Section 7.

8.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar.

8.2.1 If field measurements are being made the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movement across the electrode sensing element as indicated by drift free (<0.1 pH) readings.

8.3 If the sample temperature differs by more than 2°C from the buffer solution the measured pH values must be corrected. Instruments are equipped with automatic or manual

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(1) National Bureau of Standards Special Publication 260.

compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

8.4 After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.

9. Calculation

9.1 pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest °C.

10. Precision and Accuracy

10.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as Bias, %	Accuracy as Bias, pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

10.2 In a single laboratory (EMSL), using surface water samples at an average pH of 7.7, the standard deviation was ±0.1.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 460, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1293–65, p 178 (1976).

2.11.2 Quality Control Procedures

Quality control procedures to be used in the pH measurement of groundwaters are described below. In addition, all standardization and quality control procedures given in Method 150.1 are to be followed. The QC activities and the frequency, control limits, and correction action for each are summarized in Table 2- .

A. Calibration and Standardization

The pH meter must be calibrated daily using a minimum of two buffer solutions approximately 3 pH units apart, bracketing the expected pH range of the samples. Procedures are more fully delineated in Section 7 of Method 150.1.

B. Calibration Check

A calibration check of the pH meter is made after every tenth sample using a single buffer solution. If deviation from the calibration reading of that buffer is not less than or equal to 0.1 pH units, the pH meter must be recalibrated and all samples run since the last acceptable calibration check must be reanalyzed.

C. Replicate Analyses

One out of every ten samples must be analyzed in duplicate. A replicate is a second aliquot of a sample subjected to the complete procedure.

TABLE 2- . INTERNAL QC REQUIREMENTS--pH OF GROUNDWATER

Operation check	Frequency	Control limits	Planned corrective action
Calibration of meter	Daily before analysis of samples	Not applicable	Not applicable
Calibration check	One after every tenth sample	Deviation ≤ 0.1 pH units	Recalibrate meter Reanalyze all samples since last acceptable calibration check
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

2.12 CONDUCTIVITY

2.12.1 Analytical Procedures

The conductivity of groundwater samples is measured using procedures outlined in Method 120.1 from "Methods of Chemical Analysis of Water and Wastes," EPA-600/4-79-020. That method refers extensively to Method 205 from "Standard Methods for the Examination of Water and Wastes," 14th Edition, 1975. The latter procedure is reproduced in this section.

All quality control procedures outlined in the standard method are to be followed in these analyses.

Groundwater samples are refrigerated at 4°C until time of analysis. Just prior to conductivity measurement, the samples are allowed to warm to room temperature and are then adjusted to 25°C for analysis. If solution temperature is not 25.0 ± 0.1°C at the time of measurement, the actual sample temperature must be noted as part of the result.

Conductivity is a numerical expression of the ability of a water sample to carry an electric current. This number depends on the total concentration of the ionized substances dissolved in the water and the temperature at which the measurement is made. The mobility of each of the various dissolved ions, their valences, and their actual and relative concentrations affect conductivity.

An aqueous system containing ions will conduct an electric current. In a direct-current field the positive ions migrate toward the negative electrode, while the negatively charged ions migrate toward the positive electrode. Most inorganic acids, bases, and salts (such as hydrochloric acid, sodium carbonate, and sodium chloride) are relatively good conductors. Conversely, molecules of such organic compounds as sucrose and benzene that do not dissociate in aqueous solution conduct a current very poorly, if at all.

Freshly distilled water has a conductivity of 0.5 to 2 μmhos/cm, increasing after a few weeks of storage to 2 to 4 μmhos/cm. This increase is caused mainly by absorption of atmospheric carbon dioxide, and, to a lesser, extent, ammonia.

The conductivity of potable waters in the United States ranges generally from 50 to 1,500 μmhos/cm. The conductivity of domestic wastewater reflects to a degree the characteristics of the water supply serving the district. Some industrial wastes may have conductivites well in excess of 10,000 μmhos/cm.

Monitoring equipment is useful for conductivity measurements of water and wastewater. Commercially available instruments provide essentially continuous records of the conductivity of flowing streams. Conductivity can be recorded either by single-parameter instruments or by more elaborate monitors that also measure and record other variables such as dissolved oxygen, pH, and temperature of the stream. The sensor (or cell) may be placed in a tank through which water is pumped continuously, or placed directly in the flowing stream, depending on conditions at the monitoring site.

In order to obtain reliable results, monitoring instruments must be carefully maintained and frequently checked. Procedures for doing so depend on the nature of the streams being monitored and the characteristics of the instruments; they cannot be prescribed here in detail. Periodic comparisons of the indicated conductivity with laboratory determinations will show how frequently the sensor and intake must be cleaned. Most problems in obtaining good records with monitoring equipment are related to electrode fouling and to inadequate circulation of solutions being measured.

A number of practical applications are made of conductivity measurements, as follows:

a. Conductivity is at least as good a criterion of the degree of mineralization as the more commonly used "total dissolved solids" for assessing the effect of diverse ions on chemical equilibria, physiological effect on plants or animals, corrosion rates, etc.

b. The purity of distilled and deionized water can be checked by the determination.

c. Variations in the dissolved mineral concentration of raw water or wastewater samples can be noted quickly. Minor seasonal variations found in reservoir waters contrast sharply with the daily fluctuations in some polluted river waters. Wastewater containing significant trade wastes also may show a considerable daily variation.

d. Conductivity measurements allow an estimate of the sample size that should be used for the common chemical determinations. They also offer a means for checking the results of a chemical analysis, as described in the Introduction, Section 104C.2.

e. Conductivity measurements make possible the determination of the amount of ionic reagent needed in certain precipitation and neutralization reactions, the end point being denoted by a change in the slope of the curve resulting from plotting conductivity against buret readings.

f. The concentration (in mg/l) of dissolved ionic matter in a sample often may be estimated by multiplying the conductivity (in µmhos/cm) by an empirical factor. This factor may vary from 0.55 to 0.9, depending on the soluble components of the water and on the temperature of the measurement. Relatively high factors may be required for saline or boiler waters, whereas lower factors may apply where considerable hydroxide or free acid is present. Even though sample evaporation results in the change of bicarbonate to carbonate, an empirical factor is often derived for a comparatively constant water supply by dividing the dissolved residue by the conductivity. An approximation of the milliequivalents per liter of either cations or anions in some waters may be obtained by multiplying the conductivity (in µmhos/cm) by 0.01.

1. GENERAL DISCUSSION

The standard unit of electrical resistance (R) is the ohm (Ω). The standard unit of electrical conductance (G) is its inverse, the siemens (or the mho, (℧). Resistivity is the resistance measured between opposite faces of a rectangular prism and is reported in ohms × unit length. Conductivity is the reciprocal of resistivity and is reported in siemens per unit length. Inasmuch as specific conductance is defined as the conductance of a conductor 1 cm long and 1 cm^2 in cross-sectional area, it is properly reported in siemens and is numerically identical to conductivity in mhos/cm. For water analyses, the siemens is inconveniently large, and results are reported in microsiemens. Conductivity may also be expressed in millisiemens/meter, which is equal to 10 µmhos/cm. Report results of water tests as conductivity in terms of micromhos/centimeter.

A conductance cell and a Wheatstone bridge may be used for measuring the electrical resistance of the sample or the conductance may be measured as the ratio of electrical current through the cell to the applied voltage.

Electrolytic conductivity (unlike metallic conductivity) increases with temperature at a rate of approximately 2%/degree C. Significant errors can result from inaccurate temperature measurement. Potassium chloride solutions have a temperature coefficient of conductivity that is lower than that of the typical potable water. Sodium chloride, on the other hand, has a temperature coefficient that closely approximates that found in most waters from wells and surface sources. Note that each ion has a different temperature coefficient; thus, for precise work, the conductivity must be determined at 25.00 C.

2. APPARATUS

a. Self-contained conductance instruments: These are commercially available. Most of these instruments consist of a source of alternating current, a Wheatstone bridge, a null indicator, and a conductivity cell. Other instruments measure the ratio of alternating current through the cell to voltage across it and have the advantage of a linear reading of conductance. The instrument chosen should be capable of measuring conductivity with an error not exceeding 1% or 1 µmho/cm, whichever is the greater.

b. Thermometer, capable of being read to the nearest 0.1 C and covering the range 23 C to 27 C. An electrical thermometer having a small thermistor sensing element is convenient because of its rapid response.

c. Conductivity cell:

1) Platinum-electrode type: Conductivity cells containing platinized electrodes are available in either the pipet or the immersion form. Cell choice will depend on the expected range of conductivity and the resistance range of the instrument. Experimentally check the range for complete instrument assembly by comparing the instrumental results with the true conductances of the potassium chloride solutions listed in Table 205:1. Clean new cells with chromic-sulfuric acid cleaning mixture and platinize the electrodes before use. Subsequently, clean and replatinize them whenever the readings become erratic, when a sharp end point cannot be obtained, or when inspecton shows that any of the platinum black has flaked off. To platinize, prepare a solution of 1 g chloroplatinic acid (platinum chloride) and 12 mg lead acetate in 100 ml water. A stronger solution will reduce the time

TABLE 205:1. CONDUCTANCE OF POTASSIUM CHLORIDE SOLUTIONS AT 25°C*

Concentration M	Conductance µmhos/cm Equivalent	Conductance µmhos/cm Specific
0	149.85	
0.0001	149.43	14.94[+]
0.0005	147.81	73.90
0.001	146.95	147.0
0.005	143.55	717.8
0.01	141.27	1,413
0.02	138.34	2,767
0.05	133.37	6,668
0.1	128.96	12,900
0.2	124.08	24,820
0.5	117.27	58,640
1	111.87	111,900

*Data drawn from Robinson & Stokes.[1]

[+] Computed from equation given in Lind et al.[2]

required to platinize electrodes and may be used when time is a factor, e.g., when the cell constant is 1.0/cm or more. Immerse the electrodes in this solution and connect both to the negative terminal of a 1.5-V dry cell battery. Connect the positive side of the battery to a piece of platinum wire and dip the wire into the solution. The amount of current should be such that only a small quantity of gas is evolved. Continue the electrolysis until both cell electrodes are coated with platinum black. The platinizing solution may be saved for subsequent use. Rinse the electrodes thoroughly and when not in use keep them immersed in distilled water.

2) Nonplatinum-electrode type: Conductivity cells containing electrodes constructed from durable common metals (stainless steel among others) are widely used for continuous monitoring and field studies. Calibrate such cells by comparing the conductivity of the water being tested with the results obtained with a laboratory instrument. Determination of the cell constant with KCl may introduce a significant error if the cell and instrument are not properly designed and mated.

3. REAGENTS

a. Conductivity water: Pass distilled water through a mixed-bed deionizer discarding the first 1,000 ml. The conductivity of this water should be less than 1 µmmho/cm.

b. Standard potassium chloride, 0.0100M; Dissolve 745.6 mg anhydrous KCl in conductivity water and make up to 1,000 ml at 25 C. This is the standard reference solution, which at 25 C has a specific conductance of 1,413 µmhos/cm. It is satisfactory for most waters when using a cell with a constant between 1 and 2. For other cell constants, stronger or weaker potassium chloride solutions listed in Table 205:1 will be needed. Store in glass-stoppered pyrex bottles.

4. PROCEDURE

a. Determination of cell constant: Rinse the conductivity cell with at least three portions of 0.01 M KCl solution. Adjust the temperature of a fourth portion to 25.0±0.1 C. Measure the resistance of this portion and note the temperature. Compute the cell constant, C:

$$C = \frac{0.001413\ R_{KCl}}{1+0.0200(t-25)}$$

b. Conductivity measurement: Rinse the cell with one or more portions of the sample to be tested. Adjust the temperature of a final portion of the sample to 25.0±0.1 C. Measure the resistance of the sample and note the temperature.

5. CALCULATION

The following directions apply to the commonly used Wheatstone bridge instruments. Instruments may be calibrated to read conductivity (or conductance) directly; in that case follow the manufacturer's instructions.

a. The conductivity G, in µmhos/cm, is given by the equation:

$$G = \frac{1,000,000\ C}{R[1+0.0200(t-25)}$$

where

R = resistance of the sample, ohms,

C = cell constant, and

t = temperature, degrees C.

6. PRECISION AND ACCURACY

Three synthetic unknown samples were tested with the following results:

Conductivity µmhos/cm	No. of Results	Relative Standard Deviation %	Relative Error %
147.0	117	8.6	9.4
303.0	120	7.8	1.9
228.0	120	8.4	3.0

With satisfactory equipment, a qualified analyst should be able to obtain results within 1% of the true value.

7. REFERENCES

1. Robinson, R. A. and R. H. Stokes. 1959. Electrolyte Solutions, 2nd ed. Academic Press, New York, p. 466.
2. J. E. Lind, J. J. Zwolenik and R. M. Fuoss. 1959. Calibration of conductance cells at 25 C with aqueous solutions of potassium chloride. J. Amer. Chem. Soc. 81:1557.

8. BIBLIOGRAPHY

Jones, G. & B. C. Bradshaw. 1933. The measurement of the conductance of electrolytes. V: A redetermination of the conductance of standard potassium chloride solutions in absolute units. J. Amer. Chem. Soc. 55:1780.

2.12.2 Quality Control Procedures

Quality control requirements to be followed in the measurement of conductivity in groundwater are described in some detail below. In addition, all QC procedures that are part of the standard methods (Method 120.1 and Method 205) are to be followed in this program. A summary of QC activities, and the type, frequency, control limits and corrective action for each is given in Table 2- .

A. Standardization and Calibration

The conductivity bridge used for these measurements must be calibrated daily before analysis using KCl solutions as described in the standard methods.

B. Calibration Check

Calibration of the conductivity bridge is to be verified after every tenth sample using a standard KCl solution. The measured conductivity must not deviate from the expected value by more than ±1 percent or ±1 μmho/cm, whichever is greater. If the calibration check standard does not meet this criterion, the conductivity bridge must be recalibrated and all samples run since the last acceptable calibration check must be reanalyzed.

C. Replicate Analysis

A replicate analysis of one of every 10 samples is performed using a second aliquot of the sample. The full analytical procedure is performed on this replicate aliquot.

TABLE 2- . INTERNAL QC REQUIREMENTS--CONDUCTIVITY OF GROUNDWATER

Operation check	Frequency	Control limits	Planned corrective action
Calibration of conductivity bridge	Daily prior to analysis	Not applicable	Not applicable
Calibration check	One after every tenth sample	Deviation less than ±1 percent or ±1 µmho/cm, whichever is greater	Recalibrate conductivity bridge Reanalyze all samples run since last acceptable calibration check
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

3.0 SOIL AND SEDIMENT ANALYSIS

3.1 OVERVIEW

Soil and sediment samples collected in the Love Canal area will be analyzed for the following classes of pollutants:

3.2 Volatile organics

3.3 Semivolatile organics

3.4 Pesticides

3.5 Metals

3.6 Dioxins

Table 2-1 (Section 2.1) of this Appendix lists the specific compounds and elements of interest.

The following quality control procedures are required for all analyses.

1. Method blanks
2. Surrogates or spikes
3. Replicate analyses
4. Laboratory control standards

Specific quality control requirements are included with each procedures

3.2 VOLATILES

3.2.1 Analytical Procedures

The procedure that shall be used in this study is a modification of Method 624, Federal Register, Volume 44, No. 233, Monday December 3, 1979. The modifications which were proposed by J. N. Blazerich, Region X, are outlined below.

1. The purging chamber is a modified 40 ml screw top vial (Figure 3-1).

2. The soil or sediment sample is prepared as follows: Transfer 10 gm of the soil or sediment to the purge chamber and add 10 ml of organic-free water containing the internal standard to the sample. Attach the purge chamber to the purge and trap system.

3. Heat the chamber to 55°C and maintain this temperature while purging for 12.0 ±0.05 minutes.

4. Proceed as specified in Method 624 which appears in Section 7.4 of this Appendix.

5. Purge and trap recoveries on spiked sediment samples averaged 80 percent with an average coefficient of variation of 30 percent (Table 3-1).

6. Quality control procedures specific to this procedure are outlined in Section 3.2.2 of this Appendix.

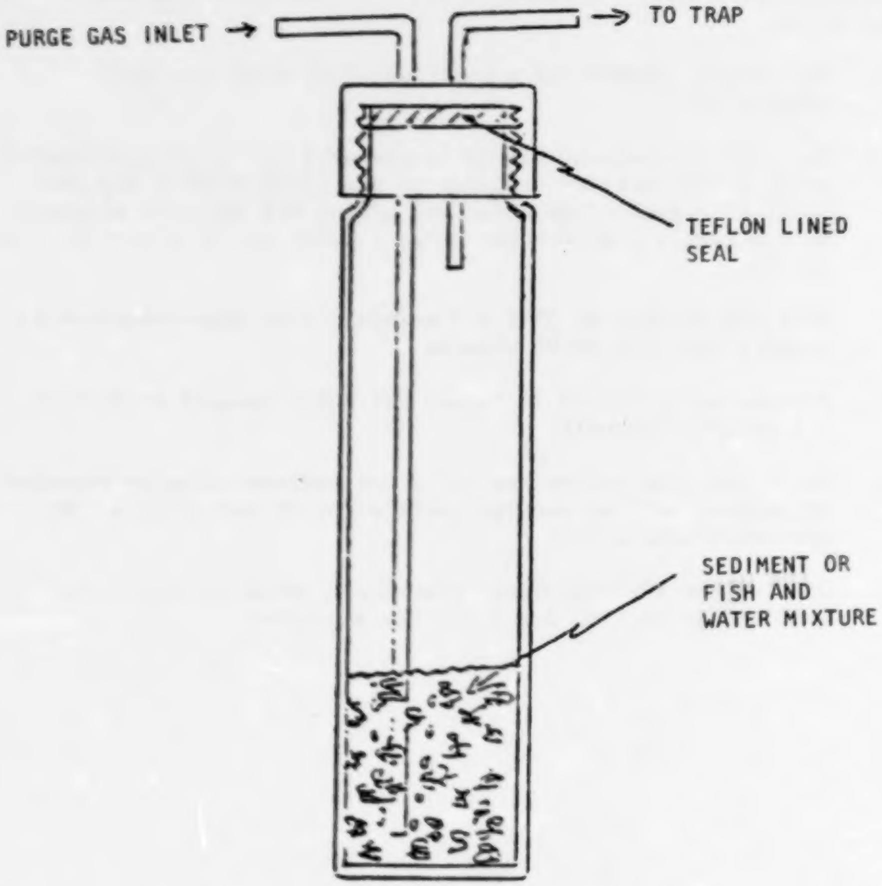
PURGE GAS INLET
TO TRAP
TEFLON LINED SEAL
SEDIMENT OR FISH AND WATER MIXTURE

Figure 3-1.

TABLE 3-1. RECOVERIES OF VOLATILE ORGANICS FROM SEDIMENT
EPA Region 10 Laboratory Branch (20 ppb level)

Compound	% Recovery	σ	C_v
Methylene Chloride	98	18	18
Chloromethane	97	16	16
1,1-Dichloroethene	87	21	24
Trans-1,2-Dichloroethene	88	24	27
Vinyl Chloride	114	27	24
1,2-Dichloroethane	90	34	38
1,1-Dichloroethane	87	17	20
Chloroethane	101	19	19
Benzene	59	24	41
Chloroform	88	19	22
Bromodichloromethane	88	37	42
1,1.2-Trichloroethane	86	34	40
1,1,2,2-Tetrachloroethane	90	27	30
Toluene	35	24	69
Bromomethane	69	15	22
Trichloroethylene	73	23	32
1,1,1-Trichloroethane	78	21	27
Chlorobenzene	37	11	30
Carbon Tetrachloride	94	28	30
Dibromochloromethane	70	29	41
1,1,2,2-Tetrachloroethene	57	21	37
Bromoform	70	29	41

Joseph N. Blazerich
3/23/79

3.2.2 Quality Control Procedures

Quality Control procedures to be followed in this analysis are described below. Included are the requirements for instrument calibration and the frequency and type of internal QC samples to be run. Each activity is described in some detail with references to standard methods made where appropriate. In addition, a summary of the frequency, control limits, and corrective action for each is given in Table 3-2.

A. Tuning of Mass Spectrometer

Procedures for tuning of the GC/MS consist of daily injection of 50 ng of the standard reference compounds 4-Bromofluorobenzene (BFB) and/or Decafluorotriphenylphosphine (DFTPP) prior to the start of sample analysis. Criteria to be met for DFTPP are given in Method 624; the criteria for BFB are given below:

4-Bromofluorobenzene Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	15 to 40% of the base peak
75	30 to 60% of the base peak
95	base peak, 100% relative abundance
96	5 to 9% of the base peak
173	less than 1% of the base peak
174	greater than 50% of the base peak
175	5 to 9% of mass 174
176	greater than 50% of the base peak
176	greater than 94% but less than 100% of 174
177	5 to 9% of mass 176

B. Calibration of GC/MS System

The GC/MS system must be initially calibrated to determine response factors using standards of compounds to be measured in this program as described in Section 6 of Method 624. After the system has been calibrated, the calibration for organic compounds must be verified at least once each day of running (8 hours) by the use of standards containing the internal standard(s). If the deviation is greater than 20 percent, the system must be recalibrated. Information regarding the verification of calibration should be recorded and provided to the Prime Contractor.

C. Internal Standards

Internal standards are added at a known concentration to every sample according to Sections 5.6 and 6.4 of Method 624. The compounds to be used as internal standards for volatile organics in soil and sediment are the following:

Dichloromethane d_2

Toluene d_8

Benzene d_6

TABLE 3-2. INTERNAL QC REQUIREMENTS-VOLATILES IN SOILS AND SEDIMENTS

Operation check	Frequency	Control limits	Corrective action planned
Tuning of mass spectrometer	Daily before analysis of samples	As specified in text	Retune spectrometer.
Method blank (reagent water)	Daily before analysis of samples	No significant concentrations found	Check analytical procedure.
Calibration check of GC/MS system	Once per 8 hours of analysis time	Deviation less than ±20 percent	Recalibrate system.
Internal standards	Added to every sample	See Sections 5.6 and 6.4 of Method 624[a]	Check analytical procedure. Analyze reference sample. Invalidate results.
Surrogate compounds	Added to every sample	±2 Standard Deviations	Check analytical procedure. Analyzes reference sample. Invalidate results.
Laboratory control standard (LCS)	One per analysis batch[b]/analysis day	Calculate as percent recovery	Check analytical procedure. Analyze second reference sample. Invalidate results.
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure. Analyze reference sample. Invalidate results.

[a] Method 624 is given in Section 7.4 of this Appendix.

[b] Analysis batch = group of samples processed as a set, usually 15 samples or less.

D. Surrogate Compounds

Surrogate organic compounds will be added at a known concentration of 100 parts per billion (100 ppb) to every environmental sample. The surrogate compounds for volatiles are the following:

Carbon tetrachloride $^{13}C_1$

1,2-Dichloroethane d_4

p-Chlorotoluene d_4

E. Laboratory Control Standards

Laboratory control standards (LCS) will be employed to identify systematic method and operator errors. The LCS is a mixture of a number of compounds of known concentration in a reference material or spiked into reagent water. For the sediment and soil analysis, one LCS will be analyzed for every 20 soil or sediment samples processed.

This LCS will consist of a one-gram aliquot of the NBS SRM 1645 (river sediment) spiked with the purgeables B Mixture provided by EPA. The B Mixture (stock solution at 10,000 μg/ml of each compound) should be spiked to result in a concentration of 100 parts per billion of each of the following compounds:

Chlorobenzene

Toluene

Benzene

Quality control data should be calculated as percent recovery of the spiked compounds. This data should be transmitted to the Prime Contractor using the appropriate Internal QC Reporting Form giving expected concentration and concentration measured for each compound.

F. Method Blanks

One method blank (reagent water) must be processed for every batch of samples and quality control tests performed using Method 624. At least one method blank must be run per work shift. The method blank must not show any signals that correspond to compounds on the Love Canal or priority pollutants list. If common laboratory contaminants are found in the method blanks, reported values for the same compounds in the environmental samples must be reduced by the amount found in the blank.

G. Replicate Analyses

Intralaboratory precision of the environmental measurements will be evaluated by the measurement of one duplicate (split) of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These results must be reported as part of the data base on the Love Canal Study.

3.3 SEMIVOLATILES

3.3.1 Analytical Procedures

Analysis of semivolatiles in soils and sediments from the Love Canal Study can be accomplished by several extraction and measurement schemes. A cross reference between methods designations and the corresponding extraction-analysis protocol is given in Table 3-3. All sample preparation procedures, including sample splitting, and weight determinations, are provided in this section. Analysis of samples by packed column GC/MS is performed using Method 625 (Federal Register, Vol. 44, No. 233, December 3, 1979) as provided in Section 7.5 of this Appendix. Exceptions and comments to Method 625 are noted below. Capillary column GC/MS procedures are given on pages 33 and 34 of this section (3.3.1).

TABLE 3-3. SOILS AND SEDIMENTS METHODS CROSS REFERENCE

Method identification	Preparation procedure	GC/MS Procedure	Number of extracts	Remarks
Method A	Procedure I	Packed column	2	B/N and Acids
Method B	Procedure I	Capillary column	2	B/N and Acids
Method C	Procedure I	Capillary column	1	Combination
Method BC	Procedure I	Capillary column	3	B/N, Acids, Combination
Method D	Procedure II	Packed column	1	
Method E	Procedure II	Capillary column	1	
Method F	Procedure III	Packed column	3	
Method G	Procedure III	Capillary column	3	

The following descriptions of the methods are given:

- Method A utilizes Preparation Procedure I to produce two extracts, one containing base/neutral compounds, the other representing the acid fraction of the sample. Analysis of these individual fractions is by packed column GC/MS.

- Method B follows Preparation Procedure I to produce two fractions as in Method A. The analysis of these individual fractions, however, is by capillary GC/MS.

- Method C also uses Procedure I to produce two fractions, base/neutrals and acids. Method C, however, requires that an aliquot of each fraction be combined and that this combined extract be analyzed by capillary GC/MS.

- Method BC extracts the sample by Procedure I and combines aliquots of the two extracts as in Method C above. Method BC, however, requires that all three fractions, base/neutrals, acids, and combination, be analyzed by capillary GC/MS.

- Method D uses Procedure II, steam distillation, to prepare the sample for analysis. Method D requires GC/MS with packed column.

- Method E also uses steam distillation, Procedure II, for sample preparation, but analysis is by capillary GC/MS.

- Method F uses Procedure III, extraction with 1:1 acetone-hexane, for sample preparation. Further isolation and clean up of the sample results in 3 extracts, each of which is analyzed by packed column GC/MS.

- Method G also uses the 1:1 acetone-hexane extraction of Procedure III for sample preparation but requires capillary GC/MS for analysis. Again, isolation and clean up of the sample results in 3 extracts for individual analysis.

Several difficulties may be encountered when analyzing semivolatile organics by the prescribed methods. These items and the required action are as follows:

- Hexachlorocyclopentadiene, analyzed by packed column GC/MS, decomposes in the injection port at the temperature required by Method 625. A second injection at a lower injection port temperature is required for quantitation should it be qualitatively identified in a sample by Method 625. This compound does not exhibit the same decomposition when analyzed by capillary column.

- Benzidine decomposes during the concentration and drying steps of Method 625. It may be observed but the concentration measurements cannot be considered reliable and a second analysis must be performed if it is detected by Method 625. Method 605 for quantitative analysis of benzidine in soil and sediment is provided in Section 7.2 of this Appendix. This additional analysis, if required, must be completed within 20 days of sample receipt. Method 605 requires slight modification for application to soil and sediment analysis.

  The sample, at pH 6-7, should be extracted with chloroform in a high speed homogenizer. This extract should then be handled as the organic solvent layer in Method 605. GC/MS analysis may be substituted for the HPLC method cited. However, all extraction and concentration techniques must be followed as per Method 605.

- Since tetrachlorotoluene standards are not readily available and due to the poor resolution of the isomers of these compounds, tetrachlorotoluenes will only be qualitatively identified and reported.

- For compounds detected which are not among those listed for quantitation, qualitative identification should be made according to the procedures provided in Section 7.7 of this Appendix.

1. Sample Splitting:

Samples received in the laboratory will have been composited and mixed in the field, and it is hoped that some degree of homogeneity will be established at the sampling site. Consequently, representative soil and sediments to be split for each of the three cleanup and isolation procedures will be provided to the laboratory. Obviously heterogeneous samples should be omitted from the phase one methods evaluation phase. In the event that many samples are apparently heterogeneous (containing large quantities of debris of varying forms, etc.) consultation with the appropriate USEPA personnel is required.

It is likely that many samples will contain volatile organic compounds, and therefore, 50 gram sample acquisition, weighing and all transferred should be accomplished rapidly. Where possible, sample containers and transfers should be accomplished to and from chilled glassware.

Obtain a 50 gram sample and weigh in a tared chilled flask. Avoid the inclusion of debris.

2. Wet Weight Determination

Wet weight determinations are usually made on sample portions that are to be analyzed for some particular constituent (or pollutant) so that constituent/sample concentrations can be indicated. Such determinations are usually made by weighing a portion of the sample (undried) that has been placed in some part of the apparatus that has been tared on a balance platform. The net weight (or the weight difference) is the sample portion wet weight.

3. Dry Weight Determination*

a. Add a portion of the sample to a tared weighing dish. Weigh and record the weight.

b. Place the weighing dish (plus sample), with the cover tipped to allow for moisture escape, in a drying oven that is set at 105°C.

c. Dry the sample to constant weight. Cool the sample in a desiccator with the weighing dish cover in place before each weighing. Record each weight. Overnight drying is usually sufficient to give a constant weight sample.

d. Calculate the dry weight fraction.

$$\frac{\text{net dry weight (g)}}{\text{net wet weight (g)}} = \text{dry weight fraction}$$

Note: Samples that contain significant amounts of volatiles that are less volatile than water may not reach constant weight with an overnight drying at 105°C.

*Caution! Certain samples could contain high levels of toxic organic compounds and therefore the furnace or oven utilized to determine dry weight should be in a hooded area.

4. Surrogate Standards Addition:

Surrogate standards will be provided by the project officer to the contractor. The surrogate standards will be stable isotope derivatives of selected compounds which have been identified at Love Canal, as well as additional compounds which will aid in the monitoring of the analysis procedures. The number and composition of surrogate standards will to some extent be dependent on compound availability. Where possible the stable isotope labeled compounds will be utilized which are mass resolved from the unlabeled compound to simplify calculations to be employed in measurement of recovery. The surrogate standards should be added to the chilled solid sample via injection of an appropriate volume of the surrogate standard mix with an appropriate sized microliter syringe. (The sample should be laced with a quantity of surrogate standard which is equivalent to 5 ppm (e.g. 250 ug/50 g sample)). The surrogate spike should be added to the solid sample in aliquots of the total volume to be added (e.g. 5, 20 ul injections from a 100 ul syringe) while manually stirring the material with a clean glass stirring rod to facilitate dispersion of surrogate compounds. It is important that the sample and sample container are chilled during the surrogate standard addition. Surrogate standard addition should be accomplished as quickly as possible to minimize the loss of the most volatile analytes covered by this method. Upon surrogate standard addition, the isolation/cleanup procedure can be initiated.

It is recognized that uniform distribution of surrogate standards in the sample will not be obtained via this procedure. Also, it is recognized that the surrogates will not mirror the properties of organic compounds which have been associated with soil or sediment samples for decades. Nevertheless, data generated from surrogate standards will serve to exemplify a "best" case recovery for the sample in question, and will provide QA/QC data for every Love Canal sample.

5A. Isolation and Cleanup - Procedure I

The following isolation and cleanup procedure was originally developed for the analysis of municipal sludges for priority pollutants by Midwest Research Institute for EMSL/Cin. This method is a modification of the aforementioned procedure which has been tested on a variety of solid sample types for priority pollutants by Southern Research Institute through funding provided by the Office of Solid Waste (OSW).

A1. Summary of Method

1.1 A 50-g sample of residual waste is extracted with methylene chloride using wet residual waste/solvent techniques aided by a high-speed homogenizer. Samples are extracted at pH 11 and again at pH 2 to extract base/neutral and acidic compounds, respectively.

A2. Interferences

2.1 Solvents, reagents, glassware, and other sample processing hardware must be thoroughly cleaned to prevent contamination and misinterpretation. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents or purification of solvents by distillation in all-glass systems may be required.

2.2 Interferences created by the samples will vary considerably from source to source, depending upon the diversity of the residual waste being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to isolate the compounds of interest from interferences and to achieve maximum sensitivity.

2.3 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used. Glassware should be sealed/stored in a clean environment immediately after drying to prevent any accumulation of dust or other contaminants.

A3. Apparatus & Material

3.1 Extracting equipment.

3.1.1 ADT tissumizer (Tekmar SDT 182EN or equivalent).

3.1.2 Centrifuge (IEC CU-5000 or equivalent).

3.1.3 Screw-capped centrifuge bottles, 200 mL (Scientific Products C4144) with TFE-lined screw caps.

3.1.4 Fleakers - 300 mL or equivalent.

3.1.4 Fleakers (or beakers) - 300 mL or equivalent.

3.1.5 Glass syring - 50 mL equipped with a 150 mm x 5 mm ID TFE tube.

3.2 Gel permeation chromatography cleanup.

3.2.1 Chromatography column - 500 mm x 19 mm ID (Scientific Products C-4670-106 or equivalent).

3.2.2 Bio-Beads S-X3, 200/400 mesh (Bio-Rad Laboratories 152-2750).

3.2.3 Glass wool.

3.2.4 Graduate cylinders - 100 mL

3.2.5 GPC Autoprep (Analytical Biochemistry Labs, Inc. 1002 or equivalent with 25 mm ID column containing 50 to 60 g of Bio-Beads S-X3.) (Optional)

A4. Reagents

4.1 Sodium hydroxide - (ACS) 10 N in distilled water.

4.2 Hydrochloric acid - (ACS) concentrated, 12 N

4.3 Sodium sulfate - (ACS) granular anhydrous; conditioned at 400°C for 4 hours and rinsed with methylene chloride (20 mL/g).

4.4 Methylene chloride - Pesticide quality (Burdick and Jackson or equivalent).

4.5 Stock standards - Prepare stock standards from EPA Priority Pollutants Kit containing the preanalyzed neat compounds (Chem Service or equivalent).

4.6 GPC calibration solutions:

a. Corn oil - 200 mg/mL in dichloromethane.

b. bis(2-ethylhexylphthalate) and pentachlorophenol - 4.0 mg/mL in dichloromethane.

A5. Calibration Standards

5.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations that will completely bracket the working range of the chromatographic system (two or more orders of magnitude are suggested). If the limit of detection (Tables

2 and 3) can be calculated as 20 ng injected, for example, prepare standards at 10 µg/mL, 100 µg/mL, 1000 µg/mL, etc. so that injections of 1-5 µL of the calibration standards will define the linearity of the detector in the working range.

A6. Sample Extraction (Base/Neutrals)

6.1 Thoroughly mix the chilled sample by homogenizing it in the sample bottle. Weigh into 250 mL centrifuge bottles a 50-g aliquot or an appropriate weight (as directed by the project officer) or predetermined by screening analyses. Add surrogate standards. (See Section 4).

6.2 Adjust the pH of the sample with 10N sodium hydroxide to a pH of 11 or greater. Mix briefly with the homogenizer to insure uniform sample pH.

6.3 Add 60 mL of methylene chloride to the sample bottle and homogenize briefly. Rinse homogenizer off with minimum of water and then about 5 - 10 mL of methylene chloride. Additional amount of methylene chloride may be added until total liquid level is near the top of the centrifuge bottle.

6.4 Centrifuge the samples at 1400 R.C.F. for 15 minutes. The mixture will separate into an aqueous layer over the methylene chloride extract. A solid cake or emulsion may form at the water-methylene chloride interface. If the emulsion interface between layers is more than one-half the size of the solvent layer, the analysts must employ a smaller sample to complete the phase separation. The optimum technique will depend upon the total solid content of the sample. Withdraw the organic extract from the centrifuge bottle with a 50-mL glass syringe that has been equipped with a 150 mm x 5 mm ID TFE tube. Discharge the extract into a 300 mL fleaker.

6.5 Add a second 60-mL volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combinine the extracts in the fleaker.

6.6 Perform a third extraction in the same manner, and dry the extract as stipulated in the Extract Drying section below.

A7. Sample Extraction (Acids)

7.1 Adjust the pH of the water, previously extracted for base-neutrals, with hydrochloric acid to a pH of 2 or less. The acid must be added slowly and with instant mixing to minimize foaming of the sample.

7.2 Extract the sample again by procedures described in Sections 6.3 to 6.6. Discard the extracted residual water aliquots.

A8. Extract Cleanup and Calibration *

8.1 Place 20-25 g of Bio-Beads S-X3 into 200 mL beaker. Cover the beads with methylene chloride and allow the beads to swell overnight before packing the column. Put a glass wool plug in the bottom of a glass chromatographic column. Transfer the swelled beads to the column and continue to rinse the packed column (450 mm x 19 mm) with methylene chloride. Add to the top of the packed column a glass wool plug followed by a layer of glass beads which will prevent the Bio-Beads from floating to the top of the eluting solvent. Wash the column with about 200 mL of methylene chloride. Just prior to exposure of the GPC packing, stop the elution with methylene chloride by closing the stopcock on the chromatography column. Discard the elute.

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* If the GPC Cleanup Method cited can be avoided, it should be because of the reduction in analysis time. A test sample can be extracted as described above and tested as delineated in Section 8.3. If the residue weight is of the order of 1-5 mg the GPC set up can in many cases be avoided.

8.2 Transfer 5 mL of the GPC calibration solution to the Bio-Beads S-X3 column. Drain the column into a 100 mL graduated centrifuge tube until the liquid is just above the surface of the GPC packing. Wash the calibration solution on the column with several 1 mL aliquots of methylene chloride. Elute the columns with 200 mL of methylene chloride and collect 10-mL fractions. Analyze the fractions for bis-(2-ethylhexyl) phthalate and pentachlorophenol by GC/FID on a 1% SP-1240 DA column. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by gravimetric determination of the residue. Plot the concentration of each component in each fraction versus the total eluent volume. Discard the first fractions that elute up to a retention volume represented by ±85% removal of the corn oil and ±85% recovery of the bis-(2-ethylhexyl)phthalate. Collect the fractions that elute up to a retention volume represented by 50 mL after the elution of pentachlorophenol. Typical parameters are to discard the first 60 mL, to collect the next 110 mL, and to wash the column with 250 mL of methylene chloride between samples.

8.3 Apply the above GPC separation procedure to an aliquot (1-4 mL) of the base/neutral or acid concentrate. The volume of concentrate submitted to GPC is determined by the total material in the concentrate. Determine a residue weight of the concentrate by placing a 1 mL aliquot on tared aluminum foil pan, allowing the solvent to evaporate, and reweighing the pan. The volume of extract submitted to GPC should not exceed the capacity of the column, approximately 200 mg.

8.4 Collect the first 60 mL of eluent in a 100 mL graduate cylinder and pass the next 110 mL of eluent through a drying column containing 60 mm of anhydrous sodium sulfate and collect in a 500 mL K-D flask equipped with 10 mL concentrator tube. Rinse the drying column with 3 25 ml portions of methylene chloride.

A9. GPC Cleaned Extract Concentration

9.1 Concentrate the GPC cleaned extract as described in Extract Concentration Procedure.

9.2 Transfer the cleaned, concentrated extract to a 6 mL serum TFE capped bottle and store at 4°C for GC/MS analysis.

5B. ISOLATION/CLEANUP - PROCEDURE II

B1. Summary

The following isolation/cleanup method has been employed by representatives of the State of New York for the analysis of clay, subsoil and first horizon samples. Some limited recovery data is available for this method for a variety of compounds which have been detected in the Love Canal soil samples. This aggressive procedure will not efficiently isolate relatively high molecular weight compounds listed in Appendix A, nor will it isolate bases. However, techniques which utilize steam distillation have been noted to yield extracts which facilitate GC/MS analysis. Also, preliminary data has shown that good recoveries can be obtained for compounds which are not thermally labile or hydrolysis prone. This technique is not equipment or manpower intensive, although it is less general than Procedure I. For these reasons we have included the methodology in Phase 1.

This method employs a steam distillation technique with a modified Nielsen - Kryger apparatus to affect isolation and cleanup in one step.

B2. Interferences

See Section 2 of Isolation and Cleanup Procedure I.

B3. Apparatus and Materials

3.1 Two liter round bottom flask with stopper.

3.2 Magnetic stirrer with Teflon stir bar.

3.3 Mofidied Neilsen - Kryger apparatus.

3.4 125 ml Erylermeyer flask with ground glass stopper.

B4. Steam Distillation Procedures State Of New York

4.1 Rinse a labeled clean 2 l round-bottomed flask with 25 ml nanograde hexane. Chill flask in an ice bath for 15 minutes.

4.2 Weigh 50 g of cold soil into the cold flask. Record weight of soil used. Keep flask tightly stopped and in ice bath when not in use.

4.3 Spike the chilled soil as delineated in the Surrogate Spiking Section.

4.4 Add 800 ml distilled water to the flask. After one minute stirring (magnetic stirrer), record pH. Add 8 ml concentrated HNO_3 to the flask dropwise, with stirring. After 10 minutes additional stirring of the stoppered flask, record final pH.

4.5 While pH is stabilizing (step 4), rinse the modified Neilsen-Kryger apparatus with nanograde hexane. Add 5 ml distilled water, then add 15 ml hexane to the solvent reservoir of the condenser.

4.6 Assemble apparatus and heat to full reflux. Stir and reflux for 1 hour.

4.7 After one hour of boiling, shut off heat and allow to cool for 10 minutes.

4.8 Drain most of the water from the solvent reservoir and discard. Drain any remaining water and add the hexane into a previously hexane-rinsed 125 ml Erlenmeyer flask equipped with a ground glass stopper. Rinse the solvent reservoir with an additional 50 ml of hexane. Add the rinse to the Erlenmeyer flask and stopper.

4.9 Measure and record the pH of the residue in the 2 l flask.

4.10 Draw off any visible water in the Erlenmeyer flask using a disposable Pasteur pipette. Discard the water. Proceed with the extract drying and concentration as outlined in Section 6.

5C Isolation/Cleanup - Procedure III

C1. Summary of Method:

The following method is described in EPA report (EPA-600/8-79-006, pg. 51), and the method has been modified to aid the isolation of low molecular weight semivolatile organic compounds which have been detected in Love Canal soil and sediment samples. A sample which has been weighed in a chilled stoppered flask and not dried is extracted with a 1:1 mixture of acetone and hexane using a mechanical tissue homogenizer or a probe type ultrasonic homogenizer. The residue is filtered with chilled glassware. The extract produced is dried and concentrated as stipulated in later section of this document or subjected to the cleanup procedure described herein.

C2. Interferences:

See Section 2 of Isolation/Cleanup Procedure I

C3. Apparatus and Materials:

Reagents and solvents should be purified as described in Method 625 or the references in Section 1.2. Standard laboratory glassware and equipment is required for this method. A stainless steel beaker is required for the extraction to preclude breakage by the mechanical or ultrasonic probe or other hard objects. The ultrasonic or high speed mechanical homogenizer (e.g., 24,000 rpm) must be constructed so that solvent vapors cannot contact oil or grease lubricated bearings.

C4 Extraction:

To the chilled 50 gram sample contained in appropriate size beaker add the surrogate standard mix as outlined in the Surrogate Standard Addition Section. Add 250 ml of 1:1 acetone-hexane, and lower the homogenizer into the beaker until it is approximately one cm from the bottom. Tilt the probe slightly about 15 degrees from vertical to prevent the solution from swirling out of the chamber while blending. Blend at maximum speed for 30 seconds. Raise the probe out of the solution and rinse it with acetone, allowing the rinsings to drain into the beaker. Filter the homogenized mixture through a 7 cm or larger medium porosity fritted glass funnel which has been chilled into a 500 ml erlenmeyer flask and which is equipped with a ground glass stopper. During extraction the Erlenmeyer flask is to be chilled in an ice bath. Two 50 ml washings should be performed on the original sample container and the filtrate. The extract should be dried as stipulated in the Extract Drying Procedure below. If the cleanup procedure is required, proceed to the next section, otherwise concentrate this extract as described in the Extract Concentration Procedure.

C5 Cleanup:

If the optical silica gel separation is to be used, concentrate the extract to 1 ml as described in the Extract Concentration Procedure. For the silica gel separation, pack activated silica gel into a glass chromatography column (2 cm I.D.) to a height of 10 cm.

To 1 ml of the extract (contained in the chilled K-D apparatus with modified micro Snyder column in place) add sufficient silica gel to adsorb the sample. Rapidly remove and replace the micro-column to add the silica gel ensuring that the extract is adequately cooled to prevent loss of the more volatile organic compounds. Evaporate the remaining solvent using the Extract Concentration Procedure. (This step is the only time evaporation should go below 0.5 ml in any procedure cited in this document). Wet the column with about 20 ml of hexane and add the chilled sample when the last of the 20 ml reaches the surface of the adsorbent. Rinse the K-D receiver with hexane and add the rinsings to the column. The K-D receiving flask should be rinsed several times with hexane and each succeeding eluent when the eluent is added to the column. Collect the fractions in chilled K-D receiving and elute the aliphatic fraction with 85 ml of hexane, the aromatic fraction with 85 ml of benzene, and the polar fraction with 1:1 methanol-methylene chloride. Concentrate each fraction to 1.0 ml

6. Extract Drying:

When the extract has not been subjected to a drying step, (Na_2SO_4, prior to cleanup for example) the following extract drying procedure will be employed.

Pour the combined extract resulting from the isolation procedure through a drying column containing three to four inches of organics free anhydrous sodium sulfate. The dried extract should be collected in a 500 ml K-D flask equipped with a 10 ml concentrator tube. The flask which originally contained the extract and the drying tube should be washed three times with 30 ml aliquots of the extraction solvent. These washes should be collected in a chilled K.D. flask.

7. Concentration:

The dried extract will be concentrated to one or five ml using the procedure stipulated as preferred in the respective RTI and GSRI report Preliminary Draft Report, Master Scheme For The Analysis Of Organic Compounds In Water, Part III: Experimental Development And Results". The initial concentration step is that recommended in the December 3, 1979 Federal Register method.

Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro-Snyder column. Prewet the column by adding approximately 1 ml of the extracting solvent through the top of the column. Place the apparatus in a 60 to 65°C water bath so that the concentrator tube is partially immersed in the water, and the lower rounded surface of the flask is bathed with water vapor. Adjust the apparatus to complete concentration to approximately 10 ml in 15 minutes. At the proper rate of distillation, the balls of the column will chatter but the chambers will not flood. When the liquid has reached an approximate volume of 4 ml, remove the apparatus from the water bath and allow the solvent to drain for at least 10 minutes while cooling. Remove the Snyder column, and rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of the solvent employed in the extraction.

The concentrator tube is then fit with a mofified micro Snyder column. Organic free nitrogen is employed to reduce the volume of the extract to approximately 5 ml or 1 ml (but not below 0.5 ml!). A Pasture pipette is inserted into the top of the Snyder column to accomplish the final concentration. The concentrator tube and the pipette are washed with approximately two 0.2 ml volumes of the extracting solvent. The final extract volume is then adjusted to 5 or 1 ml for subsequent internal standard addition and GC/MS analysis. If the extract obtained above is "clean", then a final extract volume of 1 ml is required.

If the extract is to be stored before GC/MS analysis, the extract can be transferred to an appropriately sized serum vial equipped with a Teflon-lined rubber septum and crimp cap. The extracts volume should be scored on this vial, and appropriate sample identification consistent with the quality control and chain of custody requirements must be afixed to the vial. The extracts can then be stored in the dark at 4°C.

It is possible that samples which contain high concentrations of extractable organic compounds will not be amenable for concentration to 5 ml. For extracts of this type, the final volume after concentration should be adjusted to a minimal volume which affords an extract of viscosity which allows for micro syringe sampling. In the event that numerous samples can not be concentrated to the 5 ml volume stipulated herein, the EPA project officer should be consulted for advice. Obvious remedies will likely include either starting with smaller sample size or concentration to a volume greater than 5 ml. Nevertheless the EPA project officer must be consulted for his concurrence.

8. Internal Standards Addition:

The internal standards are added to the ambient temperature extracts immediately prior to GC/MS analysis. The internal standards should be added to the extract with the solvent which was employed for concentration where possible. The project officer will provide 3 internal standard (napthalene-d_8, anthracene-d_{10} or phenanthrene-d_{10}, and chrysene-d_{12}). The internal standard should be added to 1 ml of extract to obtain a concentration of 40 ug/ml. If interferences in complex samples render the internal standard indistinguishable from noise or sample background, the analyst can increase the concentration of internal standard as required to provide a recognizable extracted ion current profile and mass spectrum for the internal standard or standards. The extract should then be reanalized. All calculations must reflect the increased extract volume and internal standard concentration.

* In the event that the internal standard anthracene-d_{10} cannot be located in a complex data file, the analyst should examine the file for the quinone of anthracene-d_{10} by viewing m/z 216, 188 and 160 at a relative retention time of approximately 1.25 ± 0.2 units (the retention time of the previously acquired data file for anthracene-d_{10} should be employed to calculate the expected scan range for the "quinone search" in the data file in which the difficulty has been encountered in internal standard location). In the event that comaximization of the aforementioned extracted ion current profiles is apparent in the complex data file in question, the project officer should be consulted prior to the addition of more internal standard.

9. GC/MS Analysis Procedures for Semivolatile Organic Compounds in Soil/Sediment Extracts of Love Canal Samples.

Two GC/MS methodologies are cited herein the first method 9A. is the methodology published in the Federal Register December 3, 1979 (Method 625). The latter methodology is a promising fused silica capillary method currently being tested by EMSL/LV and its contractors on hazardous waste samples. These tests on standards and complex samples have demonstrated that fused silica methods offer considerable advantages over packed column methods which afford increased or equivalent analysis quality while having the potential to significantly reduce GS/MS analysis costs. Additionally, in that isomeric halogenated hydrocarbons have been identified in samples at the Love Canal area, the increased resolution afforded by fused silica capillary columns will be useful in differentiating isomers in many cases. The capacity of narrow bore fused silica columns has been shown to be in excess of 2 orders of magnitude for many of the compounds listed in Appendix A. Moreover, the acidic and basic pollutants listed in Appendix A can be chromatographed at lower levels (injected) with better precision than for the former method. Also experience to date has shown that the fused silica columns can accommodate even the worst case extract without deleterious effects to the column on subsequent analysis.

For these reasons fused silica columns represent the state of the art; and the contractor could be requested by the project officer to provide analysis by the method cited below in 9B. The feasibility of this GC/MS methodology to the complex samples of Love Canal soil/sediment samples will be investigated at EMSL/LV prior to recommendation of this method. The former method (625); however, is better known , and this method has been tested as a variety of sample matrices of both complex liquid and solid origins. The greater capacity of the glass packed columns is an asset of this particular procedure.

For the reasons cited above, the extracts (2 from Procedure I, 1 from Procedure II and 3 from Procedure III) will be analyzed by the procedures cited in the December 3, 1979 Federal Register, although the project officer reserves the right to request the fused silica column methodology should testing at EMSL/LV confirm fused silica methodology on concentrated soil and sediment samples. In either case the general qualitative, quantitative and instrumental verification steps outlined in Method 625 are to be employed herein except as listed below.

1. Three internal standards will be employed in this analysis protocol to provide better interlaboratory control on the relative retention time (RRT) axis and narrower response factor variation. All RRT values and response factors should be calculated using the internal standard that elutes closest to the analyte of interest (e.g. naphalene-d_8 should be employed for the calculations for the dichlorobenzenes

listed in Appendix A). The molecular ion of the internal standards are to be utilized for these calculations (i.e. M/Z = 136,188 and 240).

2. The response factor for the surrogate standards should be determined in the usual manner. This response factor will be the value which will be utilized to determine the percent recovery for each surrogate. In the event that "extraction cross over " is observed for a surrogate compound, the sum of the recoveries for each extract will serve as the total percent recovery. The percent recovery is to be calculated for each surrogate standard as shown below:

$$\% \text{ Recovery} = \frac{C_X}{C_A} \times 100\%$$

Where C_A is the concentration of surrogate compounded added to the sample, and C_X is the concentration of the surrogate standard in the sample extract as determined by GC/MS analysis.

The percent recovery for all surrogates will be calculated along with pertinent statistics including the mean, standard deviation, and relative standard deviation for all GC/MS analysis. These statistics will be employed initially by project officer to determine the best isolation/cleanup procedure, and subsequently to monitor the data quality. Control charts must be maintained for these parameters. The ions to be employed for the surrogate compounds in the above calculations (and the inferred method 625 calculations) will be determined by the Quality Assurance Division EMSL/LV. The contractor should contact this laboratory (FTS 595-2100, Commercial (702) 798-2100) for the appropriate information.

3. Initially the response factor should be determined at three levels for the appropriate compounds in Appendix A on the appropriate column over at least 1 order of magnitude (e.g. 40-400ng or as appropriate for poorly chromatographed compounds). The response factors should be determined as outlined above using the formulas in the Federal Register Method 625.

The response factor variability for naphthalene, anthracene and chrysene will be utilized to determine when instrument (R_f) recalibrations is required once the initial response factors have been acquired and adequate precision is demonstrated, as discussed below.

The response factors for naphthalene, anthracene and crysene is to be calculated relative to the perdeutro analogue. The mean, standard deviation and relative standard deviation of these response factors should be calculated. If the relative standard deviation for any of these compounds exceeds 0.05 for initial calibration, the data is of unacceptable precision, and additional standard runs are required to establish the precision stipulated above.

Daily Response Factors for at least 1 composite standard will be acquired. Verification of the naphthalene, anthracene and chrysene response factors will be used to determine when R_f recalibration is required (at 3 levels). When the value of any of the response factors exceeds the initially determined mean value ± 1.5 times the initially determined standard deviation or when major instrument maintenance has been performed (i.e. ion source, or rod cleaning), new R_f valves must be determined at 3 levels.

All instruments must be mass calibrated and ion abundance calibrated in accordance with the Federal Register Method 625. Also, the chromatographic column verification acquisitions for pentachilorophenol or benzidine as stipulated in Method 625 must be done daily,

The following extracts produced by the Isolation/Cleanup Procedures I, II, and III should be analyzed on the columns listed below. It is likely that certain extracts will be combined (e.g. the hexane and benzene extracts for Procedure III), pending results from initial samples.

Isolation Cleanup		Column Method	
Procedure	Extract	625	Capillary
I	Acid	2	3
	B/N	1	3
II	Hexane	1	3
III	Hexane	1	3
	Benzene	1	3
	Methlenechloride acitone	2	3

Column 1:

3% SP-2250 on Supelcoport program: 50°C-2 min, 8°/min to 200°C.

Column 2:

1% SP-1240DA on Supelcoport program: 70°C-2 min, 8°/min to 200°C.

Column 3:

(See Fused Silica Capillary Column Parameters below)

9A. See Dec. 3, 1979 Federal Register Method 625

9B. Fused Silica Capillary Column Parameters

Column:

30 m x 0.25 or 0.32 SE-54 WCOT (J & W Scientific or equivalent)

Splitless Injection Parameters:

Injection mode : splitless
sweep initiation : 30 seconds
sweep flow : ≥ 12 ml/min
column flow (He) measured at atmospheric : 1.0 ml/min

Interface:

temperature : 265°C
column directly coupled to source (no transfer lines!)

Injection Volume:

1.0 µℓ with capillary style syringe

Temperature Program:

initial : 30°C for 2 minutes
program : ramp to 260°C @ 10°C/min
hold : 260°C, 15 minutes

Note:

Thermal gradient must be avoided for best analysis results. Phenomena such as "double peaking" do not constitute acceptable data. Particular attention to detail is required for to insure best results.

This includes accurate reproduction of temperatures and injection techniques.

Mass Spectral Parameters:

ionization mode/energy : Electron Impact/70eV
scan time - total : 1.0 second
mass range : 35 - 450 amu

10. GC/MS Data Verification and Reporting

GC/MS Data acquired on soil and sediment samples must be "verified" immediately after or (to the extent possible) during acquisition of each data file. For example, the operator must verify the internal standard and surrogate standard "presence" by integrating the appropriate extracted ion current profile area for each compound present in each extracts. The scan number and area of each compound must be summarized in a format which will be provided to the contractor. Moreover, data quality should be assessed by the operator to demonstrate that no saturated peaks are apparent in the total ion current profile (TIC) (except perhaps the solvent). A waiver to the above criterion could be ordered by the project officer in the event that a few compounds saturate, but low sensitivities are required for other Appendix A listed compounds, surrogates or internal standards. The project officer should be consulted for guidance in this matter. Of course if significant saturation of the TIC is observed, the sample must be diluted to an appropriate volume and reanalyzed with appropriate internal standard additions.

Prescreening extracts with equivalent GC conditions can be employed to reduce the number of GC/MS analysis or to determine the dilution volume for especially concentrated extracts. Guidance in this matter can be found in Method 625 or by consulting the project officer. In addition, surrogate percent recoveries must be reported in the GC/MS run summary sheet. Control charts will be generated for these parameters and submitted bi-weekly to the QA officer.

Data reporting format sheets will be provided by the project officer or his representative. Where possible, the contractor can utilize computer programs to assemble and hard copy the data requested above, but the format of the reports must be consistent with the data reporting forms in format and content.

Additional reporting requirements can be found in the Quality Assurance Section of this document. The project officer or quality assurance officer reserves the right to amend these requirements as needed.

Finally, due to the expected complex nature of the samples and sample concentrates direct contract with the appropriate USEPA personnel is required to satisfactorily meet the program objectives and identify the best field tested isolation and clean-up procedures for soil and sediment samples.

11. References

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2. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography--Mass Spectrometry Systems," J. W. Eichelberger, L. E. Harris and W. L. Budde, Anal. Chem. 47, 995-1000 (1975).

3. "Quality Assurance and Quality Control Procedures for Screening and Verification of Industrial Effluents for Priority Pollutants, U.S. EPA, EMSL, Cincinnati, Ohio, 45268, 1979.

4. "Development of Analytical Test Procedures for the Measurement of Organic Priority Pollutants in Sludges and Sediments," MRI Project No. 4583-A, EMSL, Cincinnati, Ohio, 45268, 1979.

5. Federal Register, 44, No. 233, 69464-69575, Dec. 3, 1979.

6. "Qantitative Aspects of Gas Chromatography/Mass Spectrometry Analysis," A. D. Sauter, L. B. Betowski, M. H. Hiatt and E. P. Meier, presented at the meeting of American Society of Mass Spectroscopy in New York, N.Y., May 26, 1980.

7. "Master Scheme for the Analysis of Organic Compounds in Water (Preliminary Draft Report), Part III: Experimental Development and Results," B. Bickford, et.al., U.S. EPA, Research Triangle Park, and J. Gebhart et.al., Gulf Southern Research Institute, New Orleans, LA. Contract No. 68-03-2704.

8. "Proposed Methods for Base/Neutral and Acids in Residual Waste, (Draft Report), Southern Research Institute, June, 1980.

3.3.2 Quality Control Procedures

Quality control procedures to be employed for the analysis of semivolatile organics in soil and sediment samples are described below. Included are the requirements for instrument calibration and the frequency and type of internal QC samples to be run. Each activity is described in some detail with reference to standard methods made where appropriate. In addition, a summary of the frequency, control limits, and corrective action for each is given in Table 3-4.

A. Quality Control Procedures

Daily measurements of the GC/MS standard reference compound Decafluorotriphenylphosphine (DFTPP) and/or p-Bromofluorobenzene (BFB) must be made using the procedures set forth in Method 625. The criteria established by Method 625 must be met and must be recorded and provided to the Prime Contractor.

B. Calibration of GC/MS System

The GC/MS system must be initially calibrated to determine response factors using standards as described in Section 6 of Method 625. After the system has been calibrated, the calibration for organic compounds must be verified at least once per day of running (8 hours) by the use of standards containing the internal standard(s). If the deviation is greater than 20 percent, the system must be recalibrated. Information regarding the verification of calibration should be provided to the Prime Contractor.

In addition, the performance of the capillary chromatographic column used in analysis methods B, C, BC, E and F must be verified by injection of a known mixture as described in Part H of this Section.

C. Internal Standards

Internal standards are added to every sample immediately prior to analysis to assist in monitoring instrument operation. For analysis of semivolatiles in soil and sediment, the internal standards are as follows:

naphthalene d_8

anthracene d_{10}

chrysene d_{12}

D. Surrogate Compounds

Surrogate organic compounds will be added at a known concentration of 250 μg/50 g sample to every environmental sample. The analytical performance, expressed as a percentage of the true values for these compounds, will be monitored. The surrogate compounds for semivolatiles will be the following:

Hexachlorobenzene $^{13}C_6$

Pentachlorophenol $^{13}C_6$

TABLE 3-4. INTERNAL QC REQUIREMENTS - SEMIVOLATILES IN SOILS AND SEDIMENTS

Operation check	Frequency	Control limits	Corrective action planned
Tuning of mass spectrometer	Daily before analysis of samples	Table 10 of Method 625[a]	Retune spectrometer.
Verify capillary column performance	Daily before analysis of samples	Tailing factor $\leq$1.5	Check analytical procedures. Analyze second reference sample. Replace column.
Method blank (reagent water)	One per analysis batch[b]/ analysis day	No significant concentrations found	Correct for blank. Check analytical procedure.
Calibration check of GC/MS system	One per 8 hours of analysis time	Deviation less than ±20 percent	Recalibrate system.
Internal standards	Added to every sample	Section 6.4 of Method 625[a]	Check analytical procedure. Analyze reference sample. Invalidate results.
Surrogate compounds	Added to every sample	±2 standard deviations	Check analytical procedure. Analyze reference sample. Invalidate results.
Laboratory control standard (LCS)	One per analysis batch[b]/ analysis day	Calculate as percent recovery	Check analytical procedure. Analyze second reference sample. Invalidate results.
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure. Analyze reference sample. Invalidate results.

[a] Method 625 appears in Section 7.5 of this Appendix.

[b] Analysis batch = group of samples processed as a set, usually containing 15 samples of less.

2-Chlorophenol $^{13}C_6$

Tetrachlorobenzene $^{13}C_6$

p-Chlorotoluene d_4

E. Laboratory Control Standards (LCS)

Laboratory control standards (LCS) will be employed to identify systematic method and operator errors. The LCS is a mixture of a number of compounds of known concentration in a reference material or spiked into samples. For the sediment and soil analysis, one LCS--one of a 5-gram aliquot of the NBS SRM 1645 river sediment--will be analyzed for every 20 sediment or soil samples processed.

Since the SRM 1645 does not contain appreciable quantities of many compounds of interest to the Love Canal study, mixtures of base/neutral and acid extractable semivolatiles must be spiked into the river sediment to provide a suitable LCS. Each mixture is provided by EPA at a concentration of 5000 μg/ml for each compound. The resultant concentration in the sediment LCS should be 5-10 ppm of the following compounds:

Base/Neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
2,4-Dinitrotoluene	2-Chlorophenol
Di-n-butyl phthalate	p-Chloro-m-cresol
Pyrene	4-Nitrophenol
N-Nitroso-di-n-propylamine	
1,4-Dichlorobenzene	

Quality control data should be calculated as percent recovery of the spiked compounds. This data should be transmitted to the Prime Contractor using the appropriate Internal QC Reporting Form specifying expected and measured concentration for each compound.

F. Method Blanks

One method blank (reagent water) must be processed through the entire laboratory analytical procedure for each set of samples extracted in a group at the same time on the same day. Normally this will be one method blank for 5 to 15 samples depending on how many samples are extracted in a given batch. The method blank must not show any signals that correspond to compounds on the Love Canal or priority pollutants list. If common laboratory contaminants; e.g., phthalate esters, are found in the method blanks, reported values for the same compounds in the environmental samples must be reduced by the amount found in the blank.

G. Replicate Analyses

Intralaboratory precision of the environmental measurements will be evaluated by the measurement of one duplicate (split) of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These results must be reported as part of the data base on the Love Canal Study.

H. Capillary Column Performance

Performance of the capillary column is to be monitored daily using the following tentative procedures:

Analysis

100 ng of pentachlorophenol and benzidine simultaneously using a 1.0 μl injection

Analysis of the Grob mixture

Criterion:

Tailing factor ≤ 1.5 for those compounds.

3.4 PESTICIDES

3.4.1 Analytical Procedures

For the analysis of soils and sediments for pesticides, the methods published in "Analysis of Pesticide Residues in Human and Environmental Samples" (revised June 1977, J. F. Thompson, Ed., U.S. Environmental Protection Agency, Health Effects Research Laboratory, RTP, NC) shall be used with the following modifications:

1. Method 608, Part II, Gas Chromatography (page 69502), Federal Register, Vol. 44, No. 233, December 3, 1979, shall be used for the GC identification of the pesticides. A copy of Method 608 is included in Section 7.3 of this Appendix.

2. All positives identified by GC shall be verified by GC/MS using the appropriate section of Method 625, Federal Register, Vol. 44, No. 233, December 3, 1979. A copy of Method 625 is included in Section 7.5 of this Appendix.

3. Soils are analyzed using the procedure entitled "Sample Preparation and Analysis of Soils and House Dust" beginning on page 2 of this section. Parts VIII and IX of this method are to be disregarded.

4. Sediments are analyzed using the procedure entitled "Sample Preparation and Analysis of Bottom Sediment," beginning on page 11 of this section. Part V of this method has been modified and Part IV of this method is to be disregarded.

5. Quality control procedures outlined in Method 608 must be followed. Additional quality control requirements for analyses are given in Section 3.4.2 of this Appendix.

SAMPLE PREPARATION AND ANALYSIS OF SOILS AND HOUSE DUST

I. INTRODUCTION:

The analytical method described below is similar in principle to the method presented in the Analytical Manual distributed at the annual Chemist's Meeting in Tucson in 1968. The main difference lies in the incorporation of the standard Mills, Onley, Gaither Florisil cleanup technique for which all laboratories have equipment and a degree of expertise in manipulation. This is preceded by percolation through an alumina column for further removal of contaminants.

II. PRINCIPLES:

Organochlorine pesticides, together with other lipid-soluble substances, are extracted from homogenized samples by continuous Soxhlet extraction with acetone-hexane. Bulk of solvent is removed by evaporation in Kuderna-Danish equipment. Interfering lipid-soluble materials are then partially removed from the extracts by successive cleanup on aluminum oxide and Florisil columns. Extracts are adjusted to appropriate concentration for determinative analysis by E.C. and F.P.D., confirming as needed by M.C. and/or T.L.C.

III. EQUIPMENT:

1. Soxhlet extraction apparatus, complete with 125-ml \$ 24/40 flask, extraction tube with \$ 24/40 lower and \$ 34/45 upper joints and Friedrichs condenser with \$ 34/45 joint. Kimble #24010 or the equivalent for the entire assembly.

2. Soxhlet extraction thimbles, paper, Whatman, 25 x 80 mm, Fisher #9-656-c or the equivalent.

3. Sieves, U. S. Standard, #10 mesh, #18 mesh and #60 mesh with top covers and bottom pans, 8" dia. x 2" depth, stainless steel.

4. Chromatographic columns, 22 x 300 mm with Teflon stopcock, without glass frit. Size #241, Kontes #420530 or the equivalent.

5. Kuderna-Danish concentrator fitted with grad. evaporative concentrator tube. Available from the Kontes Glass Company, each component bearing the following stock numbers:

    a. Flask, 250 and 500 ml, stock #K-570001.

    b. Snyder column, 3 ball, stock #K-503000.

c. Steel springs, 1/2", stock #K-662750.

d. Concentrator tubes, 10 ml grad., size 1025, stock #K-570050.

6. Modified micro-Snyder columns, 19/22, Kontes K-569251.

7. Glass beads, 3 mm plain, Fisher #11 - 312 or equivalent.

8. Evap. concentrator tubes, grad., 25 ml, ₮ 19/22, Kontes #570050.

9. Water or steam bath.

10. Glas Col heating mantles with variable autotransformers, size to match 125-ml Soxhlet flasks.

11. Filter paper, Whatman No. 1, 15 cm.

IV. REAGENTS AND SOLVENTS:

1. Acetone, pesticide quality.

2. Hexane, pesticide quality.

NOTE: Both solvents must be carefully checked for background contaminants as outlined in Section 3,C of this manual.

3. Extraction mixture - acetone/hexane, 1:1.

4. Aluminum oxide, Merck reagent grade, stock #71695 acid-washed. Prepare for use by shaking with 10% distilled water (w/w) for partial deactivation. Shelf life of 10 days if stoppered tight.

NOTE: The distilled water must be prechecked for contaminant background. If any interferences are detected, the water must be hexane extracted before use.

5. Diethyl ether - AR grade, peroxide free. The ether must contain 2% (v/v) absolute ethanol. Most of the AR grade ethyl ether contains 2% ethanol, added as a stabilizer, and it is therefore unnecessary to add ethanol unless peroxides are found and removed.

NOTE: To determine the absence of peroxides in the ether, add 1 ml of ether in a clean 25-ml cylinder previously rinsed with ether. Shake and let stand 1 minute. A yellow color in either layer indicates the presence of peroxides which must be removed before using. See Misc. Note 4 at end of procedure. The peroxide test should be repeated at weekly intervals on any single bottle or can as it is possible for peroxides to form from repeated opening of the container.

6. Eluting mixture, 6% (6+94)-purified diethyl ether - 60 ml is diluted to 1000 ml with redistilled petroleum ether,and anhydrous sodium sulfate (10-25 g) is added to remove moisture.

7. Eluting mixture, 15% (15+85)-purified diethyl ether - 150 ml is diluted to 1000 ml with redistilled petroleum ether, and dried as described above.

NOTE: Neither of the eluting mixtures should be held longer than 24 hours after mixing.

8. Florisil, 60/100 mesh, PR grade, to be stored at 130°C until used. Furnished by Perrine on order.

NOTE: (1) In a high humidity room, the column may pick up enough moisture during packing to influence the elution pattern. To insure uniformity of the Florisil fractionation, it is recommended to those laboratories with sufficiently large drying ovens that the columns be packed ahead of time and held (at least overnight) at 130°C until used.

(2) Florisil furnished by the Perrine Laboratory has been activated by the manufacturer, and elution pattern data is included with each shipment. However, each laboratory should determine their own pesticide recovery and elution pattern on each new lot received, as environmental conditions in the various laboratories may differ somewhat from that in Perrine. Each new batch should be tested with a mixture of β-BHC, aldrin, heptachlor epoxide, dieldrin, p,p'-DDE, p,p'-DDD, and p,p'-DDT, eluting the standard mixture as described in Section 5,A,(1) of this manual. Dieldrin should elute entirely in the 15% diethyl ether fraction, whereas all other compounds should be in the 6% fraction.

9. Anhydrous sodium sulfate, reagent grade granular, Mallinckrodt

Stock #8024 or the equivalent.

NOTE: When each new bottle is opened, it should be tested for contaminants that will produce peaks by Electron Capture Gas Liquid Chromatography. This may be done by transferring ca 10 grams to a 125-ml Erlenmeyer flask, adding 50 ml pet. ether, stoppering and shaking vigorously for 1 minute. Decant extract into a 100-ml beaker and evaporate down to ca 5 ml. Inject 5 µl into the Gas Liquid Chromatograph and observe chromatogram for contaminants. When impurities are found, it is necessary to remove them by extraction. This may be done using hexane in a continuously cycling Soxhlet extraction apparatus or by several successive rinses with hexane in a beaker. The material is then dried in an oven and kept in a glass-stoppered container.

V. SAMPLE PREPARATION:

1. Soils and vacuum cleaner bag dusts are analyzed in the air-dry state. If a soil sample is obviously damp, it is allowed to equilibrate its moisture content with room air before handling. Trials have shown that house dust screenings generally contain approximately 0.1% moisture, possibly more in areas of high relative humidity.

2. Vacuum cleaner bag contents are sieved on U. S. Standard #10 and #60 sieves to remove hair, fibers and large particles. The resulting "fines" are separated into sealed glass jars until analyzed. Soils are sifted on a U. S. Standard #18 sieve to remove stones and other foreign material. Store the sieved soil in a sealed glass jar until analyzed.

3. The 15-cm filter paper and the Soxhlet extraction thimbles should be preextracted with the acetone/hexane extraction solvent prior to use. This may be conveniently done by folding several sheets of filter paper and placing in the Soxhlet extractor. Allow to cycle ca 2 hours, remove and dry. Wrap in aluminum foil and store in desiccator. The thimble is similarly preextracted and may be used repeatedly with no need for reextraction as long as it remains in good physical shape.

VI. EXTRACTION:

1. Weigh sample (2 grams of soil or 1 gram of dust) onto a sheet of 15-cm filter paper. Carefully fold paper to form a half-circle with the sample in the center (along the diameter line). Fold in the ends of the half-circle towards the center, the total resulting length to be ca 70 mm; then, starting at the diameter line, roll into an approximately cylindrical shape and insert into the extraction thimble.

2. As a recovery check, another portion of the same dust (or soil) should be spiked and carried through the entire procedure. This is done as follows:

   a. Weigh exactly 3.0 grams of the soil or 2.0 grams of dust into an evaporating dish. Add sufficient hexane to make a slurry.

   b. Prepare a standard mixture of the following compounds, the concentration expressed in micrograms per milliliter:*

      Lindane-----------5.0
      Hept. Epoxide-----5.0
      Aldrin------------5.0
      p,p'-DDE----------7.5
      Dieldrin------7.5
      p,p'-DDD-----10.0
      o,p'-DDT-----10.0
      p,p'-DDT-----10.0

      *In case your testing program indicates the presence of any other compounds or metabolites, standards of these should be included.

   c. Add 1.5 ml of this mixture to the soil sample or 1.0 ml to dust. Mix gently with a glass rod and evaporate the solvent at 40°C under a nitrogen stream, stirring from time to time.

   d. After removal of the solvent, allow the spiked sample to equilibrate to room temperature and humidity, and weigh the sample for extraction as outlined above in Step 1.

3. At this point, a reagent blank should be initiated, starting with the folded filter paper and carrying through the entire extraction, cleanup and determinative procedures.

4. Place the sample, reagent blank and spiked sample thimbles into separate Soxhlet extractors. Fill the boiling flasks, each containing six glass beads, about half full with the 1:1 acetone/hexane co-solvent, assemble the extraction apparatus, position in the heating mantles and start extraction.

NOTE: Each laboratory will need to determine the setting of their voltage controller. There should be sufficient heat to result in 1 discharge cycle about every 5 minutes, or ca 60 syphon discharges in a 5-hour period. This should be an adequate number of cycles to insure complete extraction.

5. At the completion of the extraction period disassemble the extraction apparatus, rinsing the joint between flask and extractor with a few ml of hexane.

6. Assemble a Kuderna-Danish evaporator with the 250-ml K-D flask attached to a 10-ml evap. concentrator tube containing one 3-mm glass bead.

7. Transfer the extract from the 125-ml Soxhlet flask to the K-D flask, rinsing the Soxhlet flask with 3 portions of 5 ml each of hexane. Attach the Snyder column and immerse evap. concentrator tube about 1-1/2 inches into the boiling water bath. Evaporate extract down to ca 3 ml, remove from bath and cool. Extract is now ready for cleanup.

VII. ALUMINA AND FLORISIL PARTITIONING:

1. Prepare an alumina column as follows:

   a. Place a small wad of prerinsed glass wool at the bottom of a 22 x 300 mm chromatographic column.

   b. Add preextracted anhydrous Na_2SO_4 to a depth of 1/2 inch.

   c. Close stopcock and fill column with hexane.

   d. In a 50-ml grad. beaker, fill exactly to the 30 ml mark with alumina (this should be ca 30 grams). Add this slowly to the column, allowing all the alumina to settle to the bottom. Top this with a 1-inch layer of Na_2SO_4. When settling is complete, open stopcock and allow the hexane to elute through the column down to a point ca 1/8 inch above the top of the upper Na_2SO_4 layer, then close stopcock.

      NOTE: This column packing technique minimizes the density that may be obtained in dry packing. The volume of hexane specified provides sufficient column prerinse.

2. Position a second K-D flask fitted with 10-ml evap. concentrator tube under column.

3. Transfer the 3 ml of concentrated extract from the first K-D evaporation to the column. Rinse tube with three portions of 3 ml each of hexane transferring the rinsings to the column.

4. Open stopcock and add 85 ml of hexane to the column, open stopcock wide and elute into the K-D flask.

5. Concentration of the eluate from the alumina column is conducted exactly the same as outlined above in Step 7 under Sample Extraction, taking extract down to 3 ml. This extract is now ready for Florisil partitioning.

6. Florisil column: Prepare the column as described in Section 5,A,(1) of this manual under FLORISIL FRACTIONATION, Steps 1 and 2, substituting hexane for pet. ether.

7. Assemble two more K-D apparatus but with 500-ml flasks and position the flask of one assembly under the Florisil column. However, at this point use 25-ml grad. evap. concentrator tubes instead of the 10-ml size for previous concentrations.

8. Using a 5-ml Mohr or a long disposable pipet, immediately transfer the extract from the evaporator tube in Step 5, above, onto the column and permit it to percolate through. Rinse tube with two successive 5-ml portions of hexane, carefully transferring each portion to the column with the pipet.

   NOTE: Use of the Mohr or disposable pipet to deliver the extract directly onto the column precludes the need to rinse down sides of the column.

9. Commence elution with 200 ml of 6% diethyl ether in pet. ether (Fraction I). The elution rate should be ca 5 ml per minute. When the last of the eluting solvent reaches a point ca 1/8 inch from the top of the Na_2SO_4 layer, place the second 500-ml Kuderna-Danish assembly under the column and continue elution with 200 ml of 15% diethyl ether in pet. ether (Fraction II). Place both Kuderna-Danish evaporator assemblies in a water bath and concentrate extract to ca 20 ml.

   NOTE: If there is reason to suspect the presence of malathion in the sample, have a third 500-ml K-D assembly ready. At the end of the 15% fraction elution, add 200 ml of 50% diethyl ether in pet. ether (Fraction III), evaporating the eluate in the same manner.

10. Remove K-D assemblies from bath, cool and rinse ₮ joint between tube and flask with a little pet. ether. Finally, dilute both extracts to exactly 25 ml and proceed with the GLC determinative step.

    NOTE: A relatively high dilution is suggested as it has been observed that residues are generally sufficiently high to warrant this. Furthermore, the concentration of contaminants remaining after cleanup is hereby reduced.

VIII. GAS CHROMATOGRAPHY:

1. Inject 5 µl of each fraction extract into the gas chromatograph (E.C. mode) primarily to determine whether the extracts will require further adjustment by dilution or concentration.

2. When appropriate dilution adjustments have been made in the extracts and column oven is set to a known temperature, the relative retention values of the peaks on the chromatograms should be calculated. When these values are compared with the values in the printed table for the appropriate column, the operator should be able to make tentative compound identifications. Microcoulometry and/or TLC may be required for positive confirmation of some of the suspect chlorinated compounds, whereas FPD may be utilized for the organophosphate suspects.

IX. ALUMINA COLUMN ELIMINATION:

It has been reported by several field scientists analyzing house dust that the alumina cleanup can be bypassed with no ill effects. In view of the expenditure of extra time and material, a laboratory conducting monitoring studies might find it advisable to make some recovery studies eliminating this step by taking the extract mentioned in Step 7 under EXTRACTION and starting the Florisil fractionation with Step 6 of subsection VII.

TYPICAL RECOVERY DATA - Soxhlet Method

-Pesticides-

	Lindane	Hep. Epox.	p,p'-DDE	Dieldrin	p,p'-TDE	p,p'-DDT
SOILS:						
Mean percent recovery:	85.25	87.83	83.08	88.25	91.17	94.17
S.D. :	5.446	9.446	6.345	6.210	6.886	8.922
n :	12	12	12	12	12	12
HOUSE DUSTS:						
Mean percent recovery:	87.33	80.58	82.92	86.27	90.00	87.78
S.D. :	6.997	12.85	6.345	12.89	9.715	20.20
n :	12	12	12	11	12	9

SAMPLE PREPARATION AND ANALYSIS OF BOTTOM SEDIMENT

I. INTRODUCTION:

The examination of sediment from the bottom of a stream or lake provides information concerning the degree of pollution resulting from pesticides, particularly the organochlorine compounds which are not readily biodegradable. This information combined with residue data obtained by analysis of the water and tissues from resident marine life contribute in the development of an overall profile of the pesticidal contamination of a given body of water.

REFERENCES:

1. Column Extraction of Pesticides from Fish, Fish Food and Mud, Hesselberg, R. J. and Johnson, J. L., in press.
2. Sediment Extraction Procedure, Southeast Water Laboratory, EPA, Athens, Georgia, Method Number SP-8/71.

II. PRINCIPLES:

The sediment sample is partially dried and extracted by column elution with a mixture of 1:1 acetone/hexane. The extract is washed with water to remove the acetone and then the pesticides are extracted from the water with 15% CH_2Cl_2 in hexane. The extract is dehydrated, concentrated to a suitable volume, subjected to Florisil partitioning, desulfurized if necessary, and analyzed by gas chromatography.

III. EQUIPMENT AND REAGENTS:

1. Pans, approximately 14" x 10" x 2-1/2".
2. Oven, drying.
3. Muffle furnace.
4. Desiccator.
5. Crucibles, porcelain, squat form, size 2.
6. Omni or Sorvall mixer with chamber of ca 400 ml.
7. Chromatographic columns, 300 mm x 22 mm with Teflon stopcock.

8. Separatory funnels, 500 ml and 250 ml with Teflon stopcocks.

9. Filter tube, 180 mm x 25 mm.

10. Kuderna-Danish concentrator fitted with grad. evaporative concentrator tube. Available from the Kontes Glass Company, each component bearing the following stock numbers:

    a. Flask, 250 ml, stock #K-570001.

    b. Snyder column, 3 ball, stock #K-503000.

    c. Steel springs, 1/2", stock #K-662750.

    d. Concentrator tubes, 10 ml, size 1025, stock #K-570050.

11. Pyrex glass wool - preextracted with methylene chloride in a Soxhlet extractor.

12. Hot water bath, temp. controllable at 80°C.

13. Sodium sulfate, anhydrous, Baker, prerinsed or Soxhlet extracted with methylene chloride.

14. n-Hexane, pesticide quality.

15. Acetone, pesticide quality.

16. Methylene chloride, pesticide quality.

17. Acetone-hexane, 1:1.

18. Diethyl ether, pesticide quality, free of peroxides.

19. Distilled water, suitable for pesticide residue analysis.

20. Sodium sulfate solution, saturated.

21. Methylene chloride-hexane, 15% v/v.

IV. SAMPLE PREPARATION AND EXTRACTION:

1. Decant and discard the water layer over the sediment. Mix the sediment to obtain as homogeneous a sample as possible and transfer

to a pan to partially air dry for about 3 days at ambient temperatures.

NOTE: Drying time varies considerably depending on soil type and drying conditions. Sandy soil will be sufficiently dry in one day, whereas muck requires at least three days. The silt and muck sediment is sufficiently dry when the surface starts to split, but there should be no dry spots. Moisture content will be 50-80% at this point.

2. Weigh 50 gm of the partially dried sample into a 400-ml Omni-Mixer chamber. Add 50 gm of anhydrous sodium sulfate and mix well with a large spatula. Allow to stand with occasional stirring for approximately one hour.

   NOTE: As the final calculations will be made on a "bone dry" basis, it is necessary at this point to initiate the test for percent total solids in the sample being extracted for pesticide evaluation. Immediately after weighing the 50gm sample for extraction, weigh ca 5 gm of the partially dried sediment into a tared crucible. Determine the percent solids by drying overnight at 103°C. Allow to cool in a desiccator for half an hour before weighing. Determine the percent volatile solids by placing the oven-dried sample into a muffle furnace and igniting at 550°C for 60 minutes. Allow to cool in a desiccator before weighing.

3. Attach the 400-ml chamber to an Omni or Sorvall mixer and blend for about 20 seconds. The sample should be fairly free flowing at this point.

4. Carefully transfer the sample to a chromatographic column. Rinse th mixer chamber with small portions of hexane adding the rinsings to the column.

5. Elute the column with 250 ml of 1:1 acetone-hexane at a flow rate of 3-5 ml/min into a 400-ml beaker.

6. Concentrate the sample extract to about 100 ml under a nitrogen stream and at a temp. no higher than 55°C. Transfer to a 500-ml separatory funnel containing 300 ml of distilled water and 25 ml of saturated sodium sulfate solution. Shake the separatory funnel for two minutes.

Revised 6/77

7. Drain the water layer into a clean beaker and the hexane layer into a clean 250-ml separatory funnel.
8. Transfer the water layer back into the 500-ml separatory funnel and reextract with 20 ml of 15% methylene chloride in hexane, again shaking the separatory funnel for two minutes. Allow the layers to separate. Discard the water layer and combine the solvent extracts in the 250-ml separatory funnel.
9. Wash the combined solvent extract by shaking with 100 ml of distilled water for 30 seconds. Discard the wash water and rewash the extract with an additional 100 ml of distilled water, again discarding the wash water.
10. Attach 10 ml evap. concentrator tube to a 250-ml Kuderna-Danish flask and place under a filter comprised of a small wad of glass wool and ca 1/2 inch of anhydrous Na_2SO_4 in a filter tube.
11. Pass the solvent extract through the drying filter into the K-D flask, rinsing with 3 portions of ca 5 ml each of hexane.
12. Attach Snyder column to top joint of K-D flask, immerse tube in 80°C water bath and concentrate extract to 5 ml or to a lesser volume if extremely low concentration levels of pesticides are expected.

V. FLORISIL PARTITIONING:

Remove tube from water bath rinsing joint with a small volume of hexane.

Florisil column: Prepare the column as described in Section 5,A,(1) of this manual under FLORISIL FRACTIONATION, Steps 1 and 2, substituting hexane for pet. ether.

Assemble two more K-D apparatus but with 500-ml flasks and position the flask of one assembly under the Florisil column. However, at this point use 25-ml grad. evap. concentrator tubes instead of the 10-ml size for previous concentrations.

Using a 5-ml Mohr or a long disposable pipet, immediately transfer the extract from the evaporator tube in Step 5, above, onto the column and permit it to percolate through. Rinse tube with two successive 5-ml portions of hexane, carefully transferring each portion to the column with the pipet.

NOTE: Use of the Mohr or disposable pipet to deliver the extract directly onto the column precludes the need to rinse down sides of the column.

Commence elution with 200 ml of 6% diethyl ether in pet. ether (Fraction I). The elution rate should be ca 5 ml per minute. When the last of the eluting solvent reaches a point ca 1/8 inch from the top of the Na_2SO_4 layer, place the second 500-ml Kuderna-Danish assembly under the column and continue elution with 200 ml of 15% diethyl ether in pet. ether (Fraction II). Place both Kuderna-Danish evaporator assemblies in a water bath and concentrate extract to ca 20 ml.

NOTE: If there is reason to suspect the presence of malathion in the sample, have a third 500-ml K-D assembly ready. At the end of the 15% fraction elution, add 200 ml of 50% diethyl ether in pet. ether (Fraction III), evaporating the eluate in the same manner.

Remove K-D assemblies from bath, cool and rinse ₸ joint between tube and flask with a little pet. ether. Finally, dilute both extracts to exactly 25 ml and proceed with the GLC determinative step.

NOTE: A relatively high dilution is suggested as it has been observed that residues are generally sufficiently high to warrant this. Furthermore, the concentration of contaminants remaining after cleanup is hereby reduced.

VI. GAS CHROMATOGRAPHY:

Again proceed as described in Section 11A.

VII. CALCULATIONS:

1. Percent Dry Solids

$$\frac{\text{gm of dried sample}}{\text{gm of sample}} \times 100 = \text{\% Dry Solids}$$

2. Percent Volatile Solids

$$\text{gm of dried sample} - \text{gm of ignited sample} = \text{gm of volatile solids}$$

$$\frac{\text{gm of volatile solids}}{\text{gm of sample}} \times 100 = \text{\% Volatile Solids}$$

3. Concentration of Pesticide in Sediment

$$\text{\% dry solids} \times 50\ \text{gm} = \text{gm of dry sample extracted}$$

$$\frac{\text{1 of sample extract injected}}{\text{1 of sample extract}} \times \text{gm of dry sample extracted} = \text{gm of dry sample injected}$$

$$\frac{\text{ng of pesticide}}{\text{gm of dry sample injected}} = \text{ppb of pesticide}$$

VIII. SULFUR INTERFERENCE:

Elemental sulfur is encountered in most sediment samples, marine algae and some industrial wastes. The solubility of sulfur in various solvents is very similar to the organochlorine and organophosphate pesticides; therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques. The sulfur will be quite evident in gas chromatograms obtained from electron capture detectors, flame photometric detectors operated in the sulfur or phosphorus mode, and Coulson electrolytic conductivity detectors. If the gas chromatograph is operated at the normal conditions for pesticide analysis, the sulfur interference can completely mask the region from the solvent peak through aldrin.

This technique eliminates sulfur by the formation of copper sulfide on the surface of the copper. There are two critical steps that must be followed to remove all the sulfur: (1) the copper must be highly reactive; therefore, all oxides must be removed so that the copper has a shiny, bright appearance; and (2) the sample extract must be vigorously agitated with the reactive copper for at least one minute.

It will probably be necessary to treat both the 6% and 15% Florisil eluates with copper if sulfur crystallizes out upon concentration of the 6% eluate.

Certain pesticides will also be degraded by this technique, such as the organophosphates, chlorobenzilate and heptachlor (see Table 1). However, these pesticides are not likely to be found in routine sediment samples because they are readily degraded in the aquatic environment.

If the presence of sulfur is indicated by an exploratory injection from the final extract concentrate (presumably 5 ml) into the gas chromatograph, proceed with removal as follows:

1. Under a nitrogen stream at ambient temp., concentrate the extract in the concentrator tube to exactly 1.0 ml.

2. If the sulfur concentration is such that crystallization occurs, carefully transfer, by syringe, 500 µl of the supernatant extract (or a lesser volume if sulfur deposit is too heavy) into a glass-stoppered, 12-ml grad., conical centrifuge tube. Add 500 µl of iso-octone.

3. Add ca 2 µg of bright copper powder, stopper and mix vigorously 1 minute on a Vortex Genie mixer.

   NOTE: The copper powder as received from the supplier must be treated for removal of surface oxides with 6N HNO_3. After about 30 seconds of exposure, decant off acid, rinse several times with dist. water and finally with acetone. Dry under a nitrogen stream.

4. Carefully transfer 500 µl of the supernatant-treated extract into a 10-ml grad. evap. concentrator tube. An exploratory injection into the gas chromatograph at this point will provide information as to whether further quantitative dilution of the extract is required.

   NOTE: If the volume transfers given above are followed, a final extract volume of 1.0 ml will be of equal sample concentration to a 4-ml concentrate of the Florisil cleanup fraction.

Table 1. Effect of Exposure of Pesticides to Mercury and Copper

Compound	Percentage Recovery Based on Mean of Duplicate Tests Mercury	 Copper
BHC	81.2	98.1
Lindane	75.7	94.8
Heptachlor	39.8	5.4
Aldrin	95.5	93.3
Hept. Epoxide	69.1	96.6
p,p'-DDE	92.1	102.9
Dieldrin	79.1	94.9
Endrin	90.8	89.3
DDT	79.8	85.1
Chlorobenzilate	7.1	0
Aroclor 1254	97.1	104.3
Malathion, diazinon, Parathion, Ethion, Trithion	0	0

3.4.2 Quality Control Procedures

The quality control procedures to be utilized in these analyses are those described in Section 7 of Method 608. These include the analysis of method blanks and fortified or spiked water samples. Calibration and standardization procedures for the gas chromatograph are sufficiently described in Section 6 of Method 608 and will not be further discussed here. Additional QC Procedures are described below and summarized in Table 3-5.

A. Laboratory Control Standard (LCS)

Laboratory control standards (LCS) will be employed to identify systematic method and operator errors. The LCS is a concentrate of a number of compounds of known concentration in a reference material or spiked into samples. For the pesticides in soil and sediment analyses, one LCS--of a spiked five-gram aliquot of the NBS SRM 1645 river sediment--will be analyzed for every 20 soil/sediment samples processed. A standard mixture of pesticides will be provided by EPA at a concentration of 500 μg/ml for each compound. This mixture is spiked onto the SRM 1645 sediment at a final concentration of 5 to 10 ppm for use as the LCS. The compounds in the pesticides mixture are the following:

Heptachlor

Aldrin

Dieldrin

Quality control data should be calculated as percent recovery of the spiked compounds. This data should be transmitted to the Prime Contractor using the appropriate Internal QC Reporting Form giving expected and measured concentration for each compound.

B. Method Blanks

One method blank (reagent water) must be processed through the entire laboratory analytical procedure for each set of samples extracted in a group at the same time on the same day. Normally this will be one method blank for every 5-15 samples depending on how many samples are extracted in a given batch. The method blank must not show any signals that correspond to compounds on the Love Canal or priority pollutants list. If common laboratory contaminants are found in the method blanks, reported values for the same compounds in the environmental samples must be reduced by the amount found in the blank.

C. Replicate Analyses

Intralaboratory precision of the environmental measurements will be evaluated by the measurement of one duplicate (split) of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These results must be reported as part of the data base on the Love Canal Study.

TABLE 3-5. INTERNAL QC REQUIREMENTS - PESTICIDES IN SOILS AND SEDIMENTS

Operation check	Frequency	Control limits	Corrective action planned
Method blank (reagent water)	One per analysis batch[a]/ analysis day	No significant concentrations found	Correct for blank. Check analytical procedure.
Laboratory control standard (LCS)	One per analysis batch[a]/ analysis day	Calculate as percent recovery	Check analytical procedure. Analyze second reference sample. Invalidate results.
Replicate analyses	One of every 10 samples	To be determined	Check analytical procedure. Analyze reference sample. Invalidate results.

[a] Analysis batch = group of samples processed as a set usually containing 15 samples or less.

3.5 METALS

3.5.1 Analytical Procedures

Soil and sediment samples collected in the Love Canal area will be analyzed by atomic absorption spectroscopy for the following elements:

- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Chromium
- Copper
- Lead
- Mercury
- Nickel
- Selenium
- Silver
- Thallium
- Zinc

Detailed sample preparation and analysis procedures for the metals of interest are given on the following pages. Quality control requirements are found in Section 3.6.2 of this Appendix.

A. General Atomic Absorption Procedures (Except Mercury)

Soil and sediment samples are to be prepared by the techniques outlined in "Interim Methods for the Analysis of Elemental Priority Pollutants in Sludge," EPA-EMSL, Cincinnati, 1978, which is reproduced on page 3 of this Section.

Subsequent analyses are to be performed according to the AA methods detailed in "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020; these procedures are contained in Section 7.8 of Appendix B.

The following additions, deletions and comments apply in these methods.

1. The digestion procedure presented in this section is applicable to both flame and furnace analysis of all elements except mercury.
2. The use of background correction for furnace analysis to correct for nonspecific absorbance and scattered light is required. Background correction is also required for direct aspiration unless it can be shown to be unnecessary.

3. All furnace analyses shall be conducted using methods of standard additions, while noting the described limitations of its use as given in the revised manual. Also, since method of standard additions may be required for direct aspiration, verification is required to justify its omission.

4. Either plastic or glass containers shall be used for samples which will be analyzed for inorganic pollutants only. All sampling containers and labware used shall be acid-cleaned according to procedures outlined in "Methods for Chemical Analysis of Water and Waste," EPA-600/4-79-020. Soil and sediment samples shall be stored at 4°C or frozen.

5. Aliquot the samples in the following manner.

   a. Open sample container using gloves in a fume hood or glove box. Close container and return it to cold storage as soon as sample aliquots have been removed. Since all samples received may be contaminated with hazardous levels of inorganic and/or organic pollutants, appropriate safety procedures must be employed.

   b. Transfer 2 gram portions from container using a Teflon-coated scoop (avoiding any obvious rock components) to four tared, acid-cleaned 150-ml tall-form beakers and reweigh beakers to determine exact aliquot weights. Use the four aliquots as follows:

      1. Dry one aliquot at 103 to 105°C and reweigh beaker to determine the dried to undried weight ratio factor.

      2. Prepare two aliquots for analysis by AAS according to the procedures contained in "Interim Methods for the Analysis of Elemental Priority Pollutants in Sludge" which is reproduced in this section.

      3. The fourth aliquot is to be analyzed for mercury according to the procedure outlined in Part B of this Section.

B. Specific Method for Mercury in Soils and Sediments

Analysis of soil and sediment samples for mercury is to be performed according to the techniques outlined in "Mercury Recoverable from Bottom Material, Atomic Absorption, Flameless," taken from Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Book 5, Chapter A1, 1979, USGS (Stock Number 024-001-03177-9), U.S. Government Printing Office, Washington, D.C.; the method is reproduced on pages 4-7 of this Section.

INTERIM METHOD FOR THE ANALYSIS OF ELEMENTAL PRIORITY POLLUTANTS IN SLUDGE
(EMSL-CINCINNATI, DECEMBER 1978)

The described digestion procedure is for preparation of sludge samples prior to required analysis by atomic absorption. With the exception of mercury, which uses an acid-permanganate digestion previous to cold vapor analysis, this digestion is applicable to both direct aspiration or furnace analysis of all other elemental priority pollutants. These pollutants are as follow: antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn).

DIGESTION PROCEDURE

Weigh and transfer to a 125 ml conical Phillips' beaker a 1.0 gram portion of sample which has been dried at 60°C, pulverized, and thoroughly mixed. Add 5 ml of 1:1 nitric acid (HNO_3) and cover with a watch glass. Heat the sample at 95°C and reflux to near dryness. Allow the sample to cool, add 4 ml of conc. HNO_3 and again reflux to near dryness. After the second reflux step has been completed and the sample has cooled, add 1 ml of 1:1 HNO_3 and 3 ml of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken with the start of effervescence that losses do not occur or the reaction is not too vigorous. Heat until effervescence subsides and cool the beaker. Continue the addition of 30% H_2O_2 in 1 ml aliquots with warming until the effervescence is minimal or the general sample appearance is unchanged. (Note: do not add more than a total of 10 ml 30% H_2O_2).

(a) If the sample is being prepared for the furnace analysis of Sb and/or direct aspiration analysis of Sb, Be, Cd, Cr, Cu, Pb, Ni, and Zn, add 2 ml of 1:1 HCl, return the covered beaker to the hot plate and reflux for an additional 10 min. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute of 50 ml with deionized distilled water. The sample is now ready for analysis.

(b) If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Cu, Pb, Ni, Se, Ag, Tl, and Zn, or the direct aspiration analysis of Ag and Tl, add 1 ml of 1:1 HNO_3, return the covered beaker to the hot plate and reflux for an additional 10 min. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 50 ml with deionized distilled water. To prepare the analysis solution, withdraw an aliquot, add any required reagent or matrix modifier and dilute with deionized distilled water to twice the volume of the aliquot withdrawn. The sample is now diluted in 1% (V/V) HNO_3 and ready for analysis.

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

Techniques of Water-Resources Investigations of the United States Geological Survey

Chapter A1

METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

By Marvin W. Skougstad, Marvin J. Fishman, Linda C. Friedman,
David E. Erdmann, and Saundra S. Duncan, Editors

Book 5

LABORATORY ANALYSIS

3-74

Mercury, recoverable from bottom material, atomic absorption spectrometric, flameless (I–5462–78)

Parameter and Code: Mercury, recoverable from bottom material, dry wt (μg/g as Hg): 71921

1. Application

1.1 This method may be used to analyze bottom material containing at least 0.01 μg/g of mercury (5 g maximum). For samples containing more than 1.0 μg/g, use less sediment.

1.2 Bottom material samples may be analyzed by this procedure after they have been prepared as directed in Method P–0520.

2. Summary of method

2.1 The cold-vapor atomic absorption procedure is based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds, if present, are decomposed by hot (95°C) digestion with potassium permanganate and potassium persulfate in acid solution. The mercuric ions are then reduced to the elemental state with stannous chloride, and the mercury vapor subsequently removed from solution by aeration and passed through a cell positioned in the light path of an atomic absorption spectrometer.

2.2 This method is based on a procedure described by Hatch and Ott (1968) and is similar in substance to the flameless atomic absorption method in "Methods for Chemical Analysis of Water and Wastes," published by the Water Quality Office of the Environmental Protection Agency (1974).

3. Interferences

Some samples may contain volatile organic compounds that absorb radiation at 253.7 nm and that may be swept from the solution along with the mercury vapor. These constitute a positive interference and the possibility of their presence must not be overlooked.

4. Apparatus

4.1 *Absorption cell* (fig. 20). Mount and align an absorption cell (10- to 20-cm path length) in the light path of the spectrometer. Position a 60-watt lamp over the cell (10 to 15 cm) to prevent condensation of water vapor. Attach a sufficient length of tubing to the outlet of the cell and vent to a hood. Connect the inlet of the cell to the aerator with a minimum length of plastic tubing. Attach a water aspirator to the outlet of the stopcock (NOTE 1).

NOTE 1. The stopcock must remain closed during analysis and opened only briefly, between samples, to remove residual mercury vapor from the absorption cell.

4.2 *Aerator* (fig. 20).

4.3 *Atomic absorption spectrometer* and recorder.

4.4 Refer to the manufacturer's manual to optimize output of the instrument for the following parameters:

Grating ------	**Ultraviolet.**
Wavelength counter.	**253.7 nm.**
Source ------	**Mercury-vapor discharge, hollow-cathode, or electrodeless discharge lamp.**

4.5 *BOD bottle*, 300-mL capacity.

4.6 *Water bath*, 95°C.

5. Reagents

5.1 *Hydroxylamine hydrochloride-sodium chloride* solution: Dissolve 10 g $NH_2OH \cdot HCl$ and 12 g NaCl in demineralized water and dilute to 100 mL (NOTE 2). Prepare fresh daily. Alternatively 12 g hydroxylamine sulfate may be used instead of the hydroxylamine hydrochloride.

~~2-59~~ 3-75

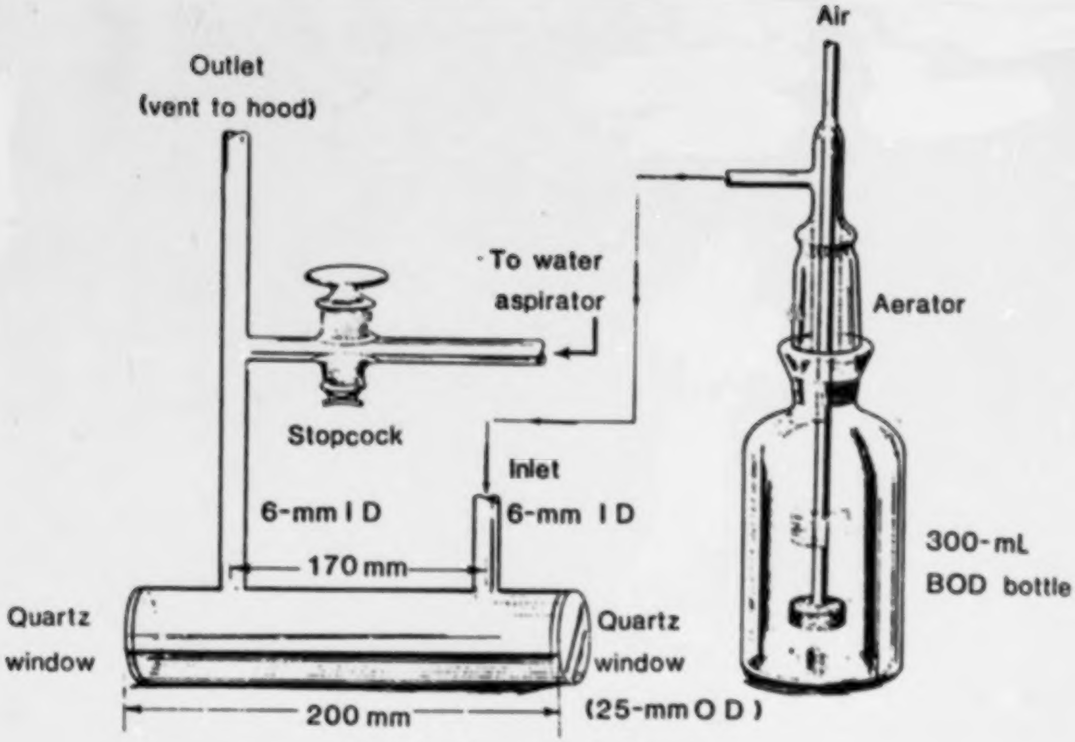

FIGURE 20.—Absorption cell and aerator.

NOTE 2. A larger volume of this reagent can be prepared and stored if it is kept refrigerated.

5.2 *Mercury* standard solution I, 1.00 mL = 100 µg Hg: Dissolve 0.1712 g $Hg(NO_3)_2 \cdot H_2O$ in demineralized water. Add 1.5 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.3 *Mercury* standard solution II, 1.00 mL = 1.00 µg Hg: Dilute 5.00 mL mercury standard solution I and 1.5 mL concentrated HNO_3 to 500 mL with demineralized water. This and the following mercury standard solutions must be prepared fresh daily.

5.4 *Mercury* standard solution III, 1.00 mL = 0.050 µg Hg: Dilute 10.0 mL mercury standard solution II and 1.5 mL concentrated HNO_3 to 200 mL with demineralized water (NOTE 3). Use this solution to prepare working standards at the time of analysis.

NOTE 3. Mercury standard solution III, 1.00 mL = 0.01 µg Hg has also been found useful. Dilute 5.0 mL mercury standard solution II and 4.0 mL concentrated HNO_3 to 500 mL with demineralized water.

5.5 *Nitric acid*, concentrated (sp gr 1.41), with low mercury content: du Pont reagent grade acid has been found to be satisfactory.

5.6 *Potassium permanganate* solution, 50 g/L: Dissolve 5 g $KMnO_4$ in demineralized water and dilute to 100 mL. Prepared fresh weekly. Store in brown glass bottle.

5.7 *Potassium persulfate* solution, 50 g/L: Dissolve 5 g $K_2S_2O_8$ in demineralized water and dilute to 100 mL.

5.8 *Stannous chloride* solution, 74 g/L: Add 22 g $SnCl_2 \cdot 2H_2O$ to 250 mL 0.25*M* H_2SO_4. Prepare fresh daily.

5.9 *Sulfuric acid*, concentrated (sp gr 1.84).

5.10 *Sulfuric acid*, 0.25*M*: *Cautiously* add 14 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

Immediately before each use, clean all glassware used in this determination by rinsing, first with warm, dilute HNO_3 (1 + 4), and then with demineralized water.

6.1 Place a weighed portion of sample containing less than 1.0 µg Hg (5 g maximum) into a 300-mL capacity BOD bottle and add approx 100 mL demineralized water.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.3 Add 5 mL concentrated H_2SO_4 and 2.5 mL concentrated HNO_3, mixing after each addition.

6.4 Add 15 mL $KMnO_4$ solution and shake. Add additional small portions of $KMnO_4$ solution, if necessary, until the purple color persists for at least 15 min.

6.5 Add 8 mL $K_2S_2O_8$ solution, mix, and heat for 2 h in a boiling-water bath or for 3 h in an-oven at 95°C.

6.6 Remove from water bath, cool, and add $NH_2OH \cdot HCl$–$NaCl$ solution in 2-mL increments to reduce the excess permanganate, as evidenced by the disappearance of the permanganate color.

6.7 Add 5 mL $SnCl_2$ solution to one sample and immediately attach the bottle to the aerator (NOTE 4). Record the maximum absorbance. After maximum absorbance has been recorded, remove the BOD bottle and open the stopcock to the vacuum. Momentarily pinch off the vent tube in order to remove residual mercury vapor from the absorption cell. Treat each succeeding sample, blank, and standard in a like manner.

NOTE 4. Use the atomic absorption compressed-air supply or a peristaltic pump to aerate the sample. Adjust the rate of air flow to approx 2 L/min.

7. Calculations

7.1 Determine the micrograms of mercury in the sample from a plot of absorbances of standards. Exact reproducibility is not obtained, and an analytical curve must be prepared with each set of samples.

7.2 Determine the concentration of mercury in micrograms per gram of air-dried bottom material sample as follows:

$$\text{Hg}\ (\mu g/g) = \frac{\mu g\ \text{Hg in sample}}{\text{sample weight (g)}}$$

8. Report

Report mercury, recoverable from bottom material (71921), concentrations as follows: less than 1.00 µg/g, nearest 0.01 g/g; 1.0 g/g and above, two significant figures.

9. Precision

It is estimated that the relative deviation (coefficient of variation) of this method is greater than 46 percent in the lower portion of the analytical range and greater than 18 percent in the mid-portion of the analytical range.

References

Environmental Protection Agency, 1974, Methods for chemical analysis of water and wastes: Cincinnati, U.S. Environmental Protection Agency, p. 118–126.

Hatch, W. R., and Ott, W. L., 1968, Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry: Analytical Chemistry, v. 40, p. 2085–2087.

3-17

3.5.2 Quality Control Procedures

Quality control requirements for the analysis of metals in soils and sediments are discussed in some detail below. These include the analysis of method blanks, replicates, and known QC samples. Instrument calibration procedures are sufficiently discussed in the standard analytical methods cited and are not further described here. In addition, selected QC requirements are summarized in Table 3-7 including the frequency, control limits, and corrective action planned for each activity.

A. Sample Spiking

For the inorganic pollutants, compounds of the actual elements (rather than surrogate compounds) are added at twice the endogenous level (with a minimum level 10 times the detection limit) to portions of the initial 10 samples of each type. If recovery for the added element is not 100 ± 15 percent, calibration by the method of additions must be used for all samples of the type involved.

B. Laboratory Control Standards

For the sediment and soil analyses, one LCS--of a 5-gram aliquot of the NBS SRM-1645 river sediment--will be analyzed for every 20 sediment or soil samples processed. A control chart must be maintained for each of the following priority pollutants with the indicated concentration as the initial mean value:

- Inorganic pollutants

Antimony	(51) mg/kg
Arsenic	(66) mg/kg
Cadmium	10.2 mg/kg
Chromium	2.96 WT %
Copper	109 mg/kg
Lead	714 mg/kg
Mercury	1.1 mg/kg
Nickel	45.8 mg/kg
Thallium	1.44 mg/kg
Zinc	1720 mg/kg

Control and warning limits (99 percent and 95 percent confidence levels, respectively) will be developed by repetitive analyses. All control charts must be monitored continuously and any value that falls beyond the 99 percent confidence control limit will require an investigation to determine the cause of the deviation. Values of environmental measurements from samples processed during that same work period will be remeasured or not reported unless a satisfactory justification is prepared. Control charts, mean values measured, and standard deviations must be reported as part of the data base from the Love Canal project.

TABLE 3-7. INTERNAL QC REQUIREMENTS - METALS IN SOILS AND SEDIMENTS

Operation check	Frequency	Control limits	Corrective action planned
Method blank (reagent water)	One per analysis batch[a]/analysis day day	No significant concentrations found	Correct for blank. Check analytical procedure.
Spiked samples	The first 10 of each type (soil or sediment) of sample	85-115% recovery of added elements	Check analytical procedure. Use method of additions.
Laboratory control standard (LCS)	One per analysis batch[a]/analysis day	As specified in text	Check analytical procedure. Analyze second reference sample. Invalidate results.
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure. Analyze reference sample. Invalidate results.

[a] Analysis batch = group of samples processed as a set, usually containing 15 samples or less.

C. Method Blanks

One method blank (reagent water) must be processed through the entire laboratory analytical procedure for each set of samples prepared in a group at the same time on the same day. Normally this will be one method blank for every 5 to 15 samples depending on how many samples are extracted in a given batch. The method blank must not show any signals that correspond to compounds on the Love Canal or priority pollutants list. If common laboratory contaminants are found in the method blanks, reported values for the same compounds in the environmental samples must be reduced by the amount found in the blank.

D. Replicate Analyses

Intralaboratory precision of the environmental measurements will be evaluated by the measurement of one duplicate (split) of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These results must be reported as part of the data base on the Love Canal Study.

3.6 DIOXINS (Tetrachlorodibenzo-p-dioxins)

3.6.1 Analytical Procedures

Soil, sediment and dust or floor sweepings samples are collected and prepared for dioxin (TCDD) analysis using the procedures given in this section. The sample is air-dried if appropriate and extracted with organic solvent. The extract is then subjected to various washing and liquid chromatographic procedures to remove organic interferences and the dioxins present in the extract determined by gas chromatography-mass spectrometry. 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is used as a standard for quantifying samples and $^{37}Cl_4$-2,3,7,8-TCDD is used as an internal standard.

The extraction techniques used for soil and sediment samples are somewhat different from those used for dust samples. Section 3.6.1 C gives extraction/cleanup procedures specific to soil and sediment samples and Section 3.6.1 D contains comparable procedures for dust or floor-sweepings samples. The extract produced is then handled as directed in Section 7.6 of this appendix. Quality Control procedures for soil, sediment and dust samples are given in Section 3.6.2.

A. Sample Handling and Preservation

TCDD is toxic and can pose grave health hazards if handled improperly. Techniques used for handling radioactive and infectious material are applicable and only qualified individuals trained in laboratory procedures and familiar with the hazards of TCDD should handle this substance. Females of childbearing age should not work with this material.

Soil, sediment or dust samples for dioxin analysis are received by the laboratory according to chain-of-custody procedures and internal chain of custody must be maintained. The samples are collected and shipped in wide-mouth glass jars with Teflon-lined lids. No chemical preservation is used; samples are maintained at 4°C until analyzed.

B. Reagents

- Potassium hydroxide, anhydrous sodium sulfate, and sulfuric acid, ACS Reagent Grade,
- Methanol, hexane, methylene chloride and benzene, "Distilled in Glass" quality,
- Petroleum ether (low boiling), Omnisone Quality from Matheson, Coleman, and Bell, or equivalent,
- WOELM basic alumina, Activity Grade 1,
- Prepurified nitrogen gas,

- Double-distilled water

- Dioxin standards can be obtained from the sources listed below:

$^{37}\mathrm{Cl}_4$-2,3,7,8-TCDD-KOR Isotopes, Cambridge, Mass.
1,2,3,4-TCDD-Analabs, Inc., North Haven, Connecticut
2,3,7,8-TCDD-Dow Chemical Co., Midland, Michigan

1,3,6,8 1,3,7,9 1,4,6,9 1,3,7,8 1,2,6,8 1,2,7,9 1,2,6,9 1,2,7,8 1,2,6,7 1,2,8,9	H. R. Buser Swiss Federal Research Station Ch-820 Wadenswil, Switzerland

C. Extraction/Cleanup Procedures for Soil and Sediment Samples

1. Remove an aliquot of the soil/sediment and air dry until a constant weight is obtained.

2. Weigh accurately a 5 gram aliquot of each dried sample and place into a 125 ml flint glass bottle (Teflon-lined screw cap).

3. Spike the sample by adding 25 ng of $^{37}\mathrm{Cl}_4$-2,3,7,8-TCDD (25 μl of a 1 ng $^{37}\mathrm{Cl}_4$-2,3,7,8-TCDD per μl benzene).

4. Add 40 ml of petroleum ether and shake for 30 minutes using a Burrell Wrist Action Shaker.

5. Transfer the extract to a clean 250 ml flint glass bottle (Teflon-lined screw cap).

6. Extract the organic solution with 50 ml of 20 percent (w/v) potassium hydroxide by shaking for 10 minutes. Allow for complete separation and remove aqueous base (bottom) layer to base waste bottle.

7. Extract the organic solution with 50 ml of doubly distilled water by shaking the sample for 2 minutes. Allow time for complete layer separation and discard the aqueous (bottom) layer.

8. Extract the organic solution with 50 ml of concentrated sulfuric acid (cautiously adding sulfuric acid) by shaking the sample for 15 minutes. Allow for complete layer separation and discard acid (bottom) layer into acid waste bottle.

9. Repeat Step 8 until acid layer is nearly transparent.

10. Extract the organic solution with 50 ml of doubly distilled water by shaking for 2 minutes. Allow for complete separation and remove aqueous (bottom) layer.

11. If the organic extract from Step 10 is colorless, proceed with Step 12. If the extract is not colorless, the following additional cleanup step is followed:

    a. Fabricate a glass Macro-column which is 20 mm x 230 mm long and is restricted to 6 mm OD on end. Pack the column with 1.0g silica, 2.0g silica containing 33 percent by weight of 1M NaOH, 1.0g silica, 4.0g silica containing 44 percent by weight of concentrated sulfuric acid, and 2.0g silica.[1]

    b. Quantitatively transfer the residue obtained in Step 10 to the column and elute the column with 45 ml hexane. Collect the hexane, concentrate this effluent and proceed with Step 12.

12. Dry the organic layer over sodium sulfate and then quantitatively transfer a portion of the organic layer to a clean test tube and reduce the volume to incipient dryness using a stream of prepurified nitrogen and while maintaining the test tube in a 55° water bath.

The dried extract should now be further cleaned up using the procedure given in Section 7.6 of this Appendix. This section also contains GC/MS analysis specifications, analytical criteria for positive TCDD results and reference material.

D. Extraction/Cleanup Procedures for Dust or Floor Sweepings Samples

1. Place a glass thimble in a Soxhlet extractor, add ∿1-2g of silica to the thimble to form a layer covering the fritted bottom of the thimble and clean the entire apparatus by performing a 2-hour extraction with benzene.

2. Remove the benzene and analyze an aliquot to ensure that all interferences and background contamination have been eliminated.

3. Accurately weigh the entire dust sample and carefully place the entire sample in the cleaned glass thimble so as not to disturb the layer of silica.

4. Spike the sample with 25 ng $^{37}Cl_4$-2,3,7,8-TCDD (add 25 µl of a solution of 1 ng $^{37}Cl_4$-2,3,7,8-TCDD per µl benzene).

5. Extract the spiked sample with 100 ml of benzene for 16 hours.

6. Remove the flask containing the extract of the sample from the Soxhlet apparatus and reduce the volume of the extract to ∿1-2 ml using a stream of prepurified nitrogen while heating the flask in a 55°C water bath.

7. Quantitatively transfer the solution to a clean 125 ml flint glass bottle, using benzene to aid in the transfer.

8. Extract the organic solution with 50 ml of 20 percent (w/v) potassium hydroxide by shaking for 10 minutes. Allow for complete separation and remove aqueous base (bottom) layer to base waste bottle.

9. Repeat Step 8 until the acid layer is nearly transparent.

10. Extract the organic solution with 50 ml of doubly distilled water by shaking the sample for 2 minutes. Allow time for complete layer separation and discard the aqueous (bottom) layer.

11. Extract the organic solution with 50 ml of concentrated sulfuric acid (cautiously adding sulfuric acid) by shaking the sample for 15 minutes. Allow for complete layer separation and discard acid (bottom) layer into acid waste bottle.

12. If the organic extract from Step 10 is colorless, proceed with Step 13. If the extract is not colorless, use the following additional cleanup step:

    a. Fabricate a glass Macro-column which is 20 mm OD x 230 mm long and is restricted to 6 mm OD on end. Pack the column with 1.0g silica, 2.0g silica containing 33 percent by weight of 1M NaOH, 1.0g silica, 4.0g silica containing 44 percent by weight of concentrated sulfuric acid, and 2.0g silica.[1]

    b. Quantitatively transfer the residue obtained in Step 10 to the column and elute the column with 45 ml hexane. Collect the hexane, concentrate this effluent and proceed with Step 13.

13. Dry the organic layer over sodium sulfate and then quantitatively transfer a portion of the organic layer to a clean test tube and reduce the volume to incipient dryness using a stream of prepurified nitrogen and while maintaining the test tube in a 55° water bath.

The dried extract should now be further cleaned up using the procedure given in Section 7.6 of this Appendix. This section also contains GC/MS analysis specifications, analytical criteria for positive TCDD results and reference material.

E. Reporting of Analytical Results

Analytical results must satisfy specific analytical criteria to be considered positive results. The criteria used by the EPA Health Effects Research Laboratory (HERL)/RTP for TCDD are given in Section 7.6 of this Appendix. Only analytical results meeting these or comparable criteria should be reported. All positive results on collected samples will be confirmed by the EPA referee laboratory. HERL/RTP.

The analytical results reported for each sample should include: sample identification, percent recovery for TCDD, minimum limits of detection for TCDDs (ng/gram), TCDDs detected (ng/gram), and comments pertaining to each analysis as necessary.

REFERENCE

1. Lamparski, L. L., T. J. Nestrick and R. H. Stehl, Anal. Chem. 51:1453 (1979).

3.6.2 Quality Control Procedures

Quality control procedures to be utilized in the analysis of TCDD are described below in some detail. In addition, the QC activities and the type, frequency, control limits and corrective action for each are summarized in Table 3-8.

A. Calibration and Standardization

A calibration curve is prepared by analyzing a series of standard solutions containing varying concentrations of 2,3,7,8-TCDD; each standard solution contains the same concentration of $^{37}Cl_4$-2,3,7-8-TCDD. The ratio of the areas of the peaks which are indicative of 2,3,7,8-TCDD and $^{37}Cl_4$-2,3,7,8-TCDD is plotted as a function of the concentration of 2,3,7,8-TCDD. Use of the internal standard technique automatically corrects the results for any losses of TCDD incurred during sample processing.

B. Calibration Check Standards/Standard Validation

Primary quantification standards containing both 2,3,7,8-TCDD and $^{37}Cl_4$-2,3,7,8-TCDD are prepared by EPA, HERL/RTP and submitted to the analytical laboratory by the Prime Contractor for use in validating the laboratory's TCDD standards.

C. Control Samples/Method Validation

Prior to actual analysis, the methodology which has been developed is tested and optimized by analyzing a series of control samples--blank soil samples to which known quantities of TCDD have been added. Generally, for samples such as those analyzed in this project, the method is deemed acceptable if 50 percent of the added TCDD is recovered and detected in the analysis. If this is not the case, then modifications are made to the method to further optimize the performance, and additional spiked samples are analyzed using the revised procedures. This is repeated until a satisfactory level of performance is obtained for the spiked samples.

D. Laboratory Control Standards (LCS)

Blank soil samples spiked with TCDD are used as laboratory control standards (LCS) to identify any systematic method or operator errors. If the recovery for the LCS is not within the acceptance limits identified during the method validation, then an entire new series of LCS analyses is repeated, and the methodology is thoroughly checked to determine the source of error. Selected Love Canal samples analyzed during any period when unacceptable QC data are obtained are also reanalyzed to ensure that these were not affected by any temporary aberrations in the methods or procedures.

E. Method Blanks

One method blank (blank soil sample) shall be carried through the sample preparation and analysis procedures to ensure that sample results can

TABLE 3-8. INTERNAL QC REQUIREMENTS--DIOXINS IN SOIL, SEDIMENT AND DUST

Operation check	Frequency	Control limits	Corrective action planned
Calibration of instrument	Daily before analysis of samples	Not applicable	Not applicable
Internal standard	Added to every sample and standard	To be determined	Report percent recovery Check analytical procedure
Calibration check	One per analysis batch[a]	To be determined	Check analytical procedure Analyze second reference standard Invalidate results and generate fresh standard curve
Method Validation	Before use of new sample cleanup/ analysis procedures	To be determined	Modify cleanup or analysis procedure
Laboratory control standard (LCS)	One per analysis batch[a]	As determined in Method validation	Check analytical procedure Analyze second reference sample Invalidate results
Method blank	One per analysis batch[a]	No significant concentrations found	Correct for blank Check analytical procedure
Analytical criteria	Each positive TCDD result	As in Section 7.6, or equivalent	Report TCDD not detected

[a] Analysis batch = group of samples processes as a set, usually containing 15 samples or less.

be corrected for compounds contributed by the reagents and chemicals used in the procedures.

F. Analytical Criteria/Confirmation of Positive Results

All positive TCDD results are tested by the criteria given in Section 7.6 or equivalent criteria, before reporting. The extracts of samples in which native TCDDs have been found are sent to the EPA referee laboratory, HERL/RTP for confirmatory analyses.

3.7 RADIOACTIVITY

3.7.1 Analytical Procedures

The soil and sediment samples are collected in 300-ml teflon-lined aluminum cans. No preservatives are added; the cans are sealed, and shipped to the analytical laboratory.

The analysis for gamma-emitting radionuclides is performed by solid-state high-resolution gamma detectors (lithium drifted germanium or intrinsic germanium detectors) connected to a tri-computer based gamma-ray spectrometer for on-line spectral acquisition and resolution. Tritium analyses are not performed on soil and sediment samples.

For other radionuclides, the radionuclides are separated from the sample by either wet-chemical, ion-exchange, or other appropriate methods and then analyzed by alpha-spectrometry or proportional beta counting, depending on the radionuclide of concern. Procedures for these measurements are not included in this Appendix.

A. Gamma-Ray Spectral Analysis

The sample, sealed in the aluminum can, is placed in a polyethylene bag and centered on the endcap of the detector for analysis. Each gamma-ray spectrum consists of 4096 channels calibrated at approximately 1/2 kev per channel. The minimum detectable concentration (MDC) for a given radionuclide is dependent on the abundance of the gamma-rays being emitted and their energy. For cesium-137 the MDC is approximately 10 picocuries (pCi) per sample or 0.04 pCi/g in soil and sediment samples.

3.7.2 Quality Control Procedures

Quality control procedures applicable to gamma-ray spectrometry of soil and sediment are described below. The quality control procedures and their frequencies are summarized in Table 3-9.

A. Calibration Standard

All radionuclide standards used in the gamma-ray spectrometry analyses are traceable to NBS. The standards are prepared and placed in the appropriate geometry by the Quality Assurance Division of the Environmental Monitoring Systems Laboratory-Las Vegas.

B. Backgrounds

For gamma-ray spectral analysis background spectra are acquired once each week.

C. Replicate Analysis

Intralaboratory measurement precision will be evaluated from the results of duplicate measurements on one of every 10 samples. The duplicate for gamma-ray measurements is the original sample.

D. Control Charts

Control charts are maintained for gamma-ray spectrometry. Plotted are background, standard's activity, efficiency, and full width of the photopeak at 1/2 maximum height.

TABLE 3-9. INTERNAL QC REQUIREMENTS - RADIOACTIVITY IN SOILS AND SEDIMENTS

Analysis	Operation check	Frequency	Control limits	Planned corrective action
Gamma	Background	Weekly	±3 standard deviations	Clean detector Check procedures Check data Possibly recalculate results
	Energy calibration	Daily before start of analyses	Subjective	Recalibrate Check procedures Check electronics Check previous day's data
	Efficiency calibration	As needed		Analyze standard Possibly reanalyze samples Recalibrate
	Participation in cross check programs	Bi-monthly, quarterly	±3 standard deviations	Check procedures Recalibrate
	Replicate analysis	One of every 10 samples	±3 standard deviations	Check procedures Analyze standard Possibly reanalyze samples

4.0 BIOTA ANALYSIS

4.1 OVERVIEW

This section includes the procedures for chemical analysis of the indicated biological specimens for the pollutant classes listed and an Interferon bioassay procedure:

4.2 Semivolatiles and Pesticides in Animal Tissue--Mouse, crayfish and earthworm tissue will be analyzed.

4.3 Volatile Organics in Foddstuffs--Potatoes and oatmeal will be analyzed.

4.4 Metals in Hair--Hair from dogs and mice will be analyzed.

4.5 Metals in Vegetation--Silver maple or other green tree leaves will be analyzed.

4.6 Interferon--Mouse cells will be assayed.

Table 2-1 (Section 2.1) of this appendix lists the specific compounds for chemical analysis; metals are listed under "Inorganics." Specific quality control requirements are included with each procedure as are the sample handling and preservation techniques to be used with each sample type.

4.2 ORGANIC COMPOUNDS

4.2.1 Analytical Procedures

The sample preparation and analysis procedures to be utilized for measurement of organic compounds in adipose tissue in the Love Canal Study are delineated below. Prior to the start of analysis, all reagents must be checked for purity as described under Quality Control Procedures.

A. Sample Handling and Preservation

Adipose tissue samples are frozen and must remain frozen until the initiation of analysis. Storage time of the frozen tissue samples must not exceed fourteen (14) days.

B. Sample Preparation

1. Put dry ice into a small laboratory blender to completely cover the blades. Homogenize the dry ice for 30 seconds. Add 5 g of tissue sample (weighed to the nearest 10 mg) to the blender along with more dry ice. Wait several minutes for the sample to freeze.

2. Homogenize for at least 2 minutes, or until the mixture is free of lumps, add 25 g of anhydrous sodium sulfate, homogenize for two more minutes, and pour the contents onto an aluminum foil sheet. Homogenize additional dry ice and 10 g of sodium sulfate and transfer this to the same aluminum foil. Mix the tissue, sodium sulfate, and dry ice on the foil with the spatula, fold the aluminum foil into the form of an envelope and place in an organics-free freezer at -15°C for 8 to 12 hours. The dry ice will sublime.

3. Prepare for the next step (No. 4) by obtaining tare weights on suffucient Kuderna-Danish (K-D) concentrator tubes for the analysis batch. This can be accomplished by placing the glass-stoppered concentrator tube in a beaker and weighing both pieces of glassware. This combination of beaker and tube constitutes a tared K-D. Final weight, and subsequently the net sample weight, are determined using the same beaker, tube, and stopper after concentration of the extract in Step 4.

4. Extract the residue in a 50-ml soxhlet with 50 ml of a 1:1 (v/v) mixture of acetone and hexane for 8 hours. Cool and transfer the extract to the tared K-D apparatus from Step 3 above and concentrate to about 4 ml. Place a modified micro Snyder column on the concentration tube and evaporate the solvent with a gentle stream of dry nitrogen, weigh the resulting oil, and dilute it with methylene chloride to a concentration of 100 mg/ml.

5. Inject the total amount of diluted extract, in 5-ml aliquots, into a gel permeation chromatograph equipped with a 2.5 x 50 cm column packed with BIO-RAD SX-3 beads. Elute each 5-ml aliquot with 225 ml of methylene chloride, at a flow rate of 3.5 ml per minute, and discard the first 160 ml of each eluate (this contains the neutral oils and fats). Collect the balance (about 65 ml) of each eluate from each aliquot in the same 500-ml KD flask.

6. Concentrate the combined eluate--containing the organics of interest--to 5 ml. If desired, analysis as outlined in Section C may be performed at this point provided the extract is further concentrated to 1 ml; however, if the resulting analytical data indicate that further clean-up is required, the extract must be diluted to 5 ml and the remaining clean-up step performed, as follows:

   - Equilibrate the gel permeation system of Step 5 with a 1:1 mixture of cyclohexane-methylene chloride. Inject the 5 ml of concentrated combined eluate and elute with 300 ml of 1:1 cyclohexane-methylene chloride at 3.5 ml per minute. Again discard the first 160 ml which contains the residual lipid material. The remaining eluate may be divided into 3 to 10 fractions or collected as a single fraction. Concentrate each fraction to 0.1 - 1 ml in a K-D apparatus.

C. Analysis

Analyze the resulting extract by capillary column gas chromatography using Hall (halogen mode) detection or by capillary column gas chromatography-mass spectrometry (GC/MS). Column specifications, chromatographic conditions and mass spectrometer operation for the latter method are as follows:

Column: 30 meter fused silica SE-54 wall coated open tubular capillary column.

Splitless Injection Parameters:

Injection mode	splitless
sweep initiation	30 seconds
sweep flow	≥12 ml/min
column flow (He) measured at atmospheric pressure	1.0 ml/min

Interface:

temperature	265°C

Injection Volume

1.0 μℓ with capillary style syringe

Temperature Program:

initial : 30°C for 2 minutes
program : ramp to 260°C @ 10°C/min
hold : 260°C, 15 minutes

Note:

Thermal gradient must be avoided for best analysis results. Phenomena such as "double peaking" do not constitute acceptable data. Particular attention to detail is required to ensure best results. This includes accurate reproduction of temperature and injection techniques.

Mass Spectrometer Operation:

Electron energy : 70 volts
Mass range : 35 to 450 amu
Scan time : 1 second or less

Performance criteria to be met by the mass spectrometer and the capillary column are discussed under Quality Control Procedures. Mass spectrometer operation is primarily based on the requirements of Method 625, Federal Register, Vol. 44, No. 233, December 3, 1979, pp. 69540-69552. A copy of Method 625 is provided in Section 7.5 of this Appendix.

For compounds to be monitored at Love Canal which are not included in Method 625, the following data on characteristic ions are provided:

CHRACTERISTIC IONS FOR COMPOUNDS NOT INCLUDED IN METHOD 625

	EI ions			Primary ions
1,2,3-trichlorobenzene	180	182	184	180
1,3,5-trichlorobenzene	180	182	184	180
2,4-dichlorotoluene	125	160	162	160
pentachloronitrobenzene	249	293	295	293
2,4,6-trichloroaniline	195	197	199	195
4-chlorobenzotrifluoride				
1,2,3,4-tetrachlorobenzene	214	216	218	214
1,2,4,5-tetrachlorobenzene	214	216	218	214
tetrachlorotoluenes (18 isomers)				
3-chlorophenol	65	128	130	128
4-chlorophenol	65	128	130	128
2,3,6-trichlorophenol	196	198	200	196

4.2.2 Quality Control Procedures

Quality Control procedures to be followed in these analyses are described below. Included are the requirements for instrument calibration and the frequency and type of internal QC samples to be run. Each activity is described in some detail with references to standard methods made where appropriate. Quality Control procedures are summarized in Table 4-1.

A. Reagent Purity

The quality of all solvents used shall be verified by GC analysis of reagent blanks prior to the extraction of the samples. If impurities are found, the solvents shall be redistilled before use in an all-glass distillation apparatus such that only approximately 80 percent of the solvents are recovered and the 20 percent remaining in the still pot are discarded. The anhydrous sodium sulfate shall be extracted with a 1:1 (v/v) mixture of methylene chloride and acetone in a soxhlet extractor for 8 hours, air dried, and heated to 120°C in an oven for 4 hours. Glassware used for blanks, spikes, and samples shall be washed with detergent, rinsed with tap water, rinsed with distilled water, air dried, and heated in a muffle furnace to 300°C for 1 hour.

B. Tuning of Mass Spectrometer

Daily measurements of the GC/MS standard reference compounds Decafluorotriphenylphosphine (DFTPP) and/or p-Bromofluorobenzene (BFB) must be made using the procedures set forth in Method 625. The criteria established by Method 625 must be met and must be recorded and provided to the Prime Contractor.

C. Calibration of GC/MS System

The GC/MS system must be initially calibrated to determine response factors using standards as described in Section 6 of Method 625. After the system has been calibrated, the calibration for organic compounds must be verified at least once each day of running (8 hours). If the deviation is greater than 20 percent, the system must be recalibrated. Information regarding the verification of calibration should be recorded and provided to the Prime Contractor.

D. Method Blanks

One method blank (reagent water) must be processed through the entire laboratory analytical procedure for each set of samples extracted in a group at the same time on the same day. Normally this will be one method blank for every 5 to 15 samples depending on how many samples are extracted in a given batch. The method blank must not show any signals that correspond to compounds on the Love Canal or priority pollutants list. If common laboratory contaminants are found in the method blanks, reported values for the same compounds in the environmental samples must be reduced by the amount found in the blank.

TABLE 4-1. INTERNAL QC REQUIREMENTS--ORGANIC COMPOUNDS IN BIOTA

Operation check	Frequency	Control limits	Planned corrective action
Tuning of mass spectrometer	Daily before analysis of samples	Table 10[a] of Method 625	Retune spectrometer
Reagent blank	All solvents prior to initiation of program	No significant concentrations found	Redistill solvents recovering only 80 percent
Method blank	One per analysis batch[b]/ analysis day	No signficant concentrations found	Correct for blank Check analytical procedure
Check calibration of GC/MS system	Once per 8 hours of analysis time	Deviation less than 20 percent	Recalibrate system
Repeated extraction	One of every 5 samples extracted	To be determined	To be determined
Replicate analysis	One of every 10 samples analyzed	To be determined	To be determined

[a] Method 625 appears in Section 7.5 of this Appendix.

[b] Analysis batch = group of samples processed as a set, usually containing 15 samples or less.

E. Repeated Extractions

Every fifth sample prepared will undergo a second complete extraction procedure, beginning with the soxhlet extraction, to determine how completely the initial procedure extracted the organic compounds of interest contained in the sample. Results of these second analyses are to be recorded and transmitted to the Prime Contract for inclusion in the Love Canal data base.

F. Replicate Analyses

Intralaboratory precision of the environmental measurements will be evaluated by the measurement of one duplicate (split) of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method.

4.3 VOLATILE ORGANICS IN FOODSTUFFS

4.3.1 Analytical Procedures

Selected foodstuffs from the Love Canal area are analyzed for the volatile organic compounds specified in Table 2-1 (Section 2.1) according to the procedures described below. Preparation procedures for each material are given along with the analytical method used for both.

Foods collected for analysis are wrapped carefully in aluminum foil in the field and placed in glass jars with teflon cap liners. Samples are refrigerated at 4°C for shipment and must be maintained at 4°C until the time of analysis.

A. Preparation of Laboratory Glassware

Prior to use in these analyses, apparatus such as headspace vials and gas tight syringes must be baked to remove volatile compounds. Unassembled parts of the headspace vials (or alternative screw-top vials) including vial, crimp or screw-top, and teflon-septum are baked under vacuum in a vacuum oven for 5 minutes at 90°C and are allowed to cool to room temperature prior to adding acid and sample.

Gas tight syringes may be baked while samples are digesting. Shortly (7-10 minutes) before the digestion procedure is complete, remove the plunger from a 5- or 10-ml precision gas syringe. Place the syringe tube, needles, and plunger in a vacuum oven and bake for 5 minutes at 90°C under vacuum. Avoid overheating as teflon elements in the syringe may flow and lose their integrity. Remove vacuum, assemble syringe parts, wearing clean cotton gloves, and replace assembled syringe into the 90°C oven until ready to use.

B. Sample Preparation and Digestion

The following procedure is to be used for preparation of potatoes or other vegetables for volatiles analysis:

Rinse whole vegetables visibly free of surface soil or debris with distilled water and blot dry with clean paper toweling. Remove a sample (approx. 5 grams) from the surface of the vegetable (to a depth of 1/8") which includes the skin. Working quickly to minimize sample warming, finely mince the sample with a clean knife or scapel; immediately transfer into a tared 25-ml crimp-top headspace vial (or small screw-top vial) with a teflon-sealed septum containing 15-ml of 10% sulfuric acid (conc. H_2SO_4 and distilled water, 1:10); seal; and weigh to the nearest 10-mg.

The preparation procedure used for cereal grains such as oatmeal or dry cereal products is as follows:

Approximately 5-grams of sample material are removed, weighed to the nearest 10 milligrams, and transferred to a 25-ml crimp-top headspace vial (or small screw-top vial) with a teflonsealed septum along with 15-ml of 10% sulfuric acid (conc. H_2SO_4 and distilled water, 1:10) and sealed. High bulk materials may have to be gently tamped with a clean glass rod to compress their volume.

Digestion of the foodstuffs proceeds by placing the sealed vials, containing sample and the digestion mixture, into a 90°C water bath for one (1) hour. The vial is not allowed to cool prior to removal of the headspace gas sample.

C. Analysis

Using a gas-tight syringe and digestion vial, both at the 90°C temperature to which they were heated, draw a 2-ml headspace gas sample from the vial. Immediately inject the sample directly onto the column of a gas chromatograph equipped with a Hall (halogen specific) detector. Column specifications and operating conditions are as follows:

Column: 8 ft. x 0.1 inch ID stainless steel or glass column

Packing: Carbopack B 60/80 mesh coated with 1% SP-1000

Carrier gas: Helium

Flow rate: 40-ml/minute

Temperature Program:

Initial - 45°C, hold for 3 minutes

Ramp - 8°C/min

Final - 220°C, hold for 15 minutes

D. Calculations

The GC must be calibrated daily, as specified in the accompanying quality control procedures, using standards of the compounds of interest. The concentration of individual compounds in the headspace gas sample is determined from calibration plots of concentration (μg/l) vs. peak height or area units. This concentration must then be correlated to the concentration of each compound in the food material. In order to perform this calculation, it is necessary to determine the total head space in the vial. One means of doing this is, after analysis, to fill the headspace vial with distilled water from a graduated pipet, recording the volume of liquid added as the headspace volume. An alternative procedure may be utilized with the prior approval of the technical monitor. Caution must be observed in opening and handling the digested samples owing to the possible hazardous nature of the compounds which may be present in the sample and also due to the presence of sulfuric acid in the digest.

Concentrations of compounds in the foodstuffs are calculated as follows:

$$C_F = C_{HS} \left(\frac{V_{HS}}{W_F} \right)$$ where

C_F = concentration in the foodstuff (μg/g)

C_{HS} = concentration in the headspace (μg/l)

V_{HS} = volume of headspace (l)

W_F = weight of footstuff digested (g)

4.3.2 Quality Control Procedures

Quality control procedures to be used in the analysis of volatile organics in foodstuffs are described below. Included are a description of instrument calibration procedures and the frequency and type of QC samples to be run. In addition, control limits and corrective action are summarized in Table 4-2.

A. Calibration and Standardization

Calibration of the gas chromatograph (GC) will be established daily by the injection of standards of the compounds of interest at three (3) concentration levels. Calibration checks are run with a single concentration mixed standard for every 8 hours of analysis. If deviation from the standard curve is greater than ±20 percent, the system must be recalibrated. Information regarding the verification of calibration must be recorded and provided to the Prime Contractor. Injection of these standard compounds is also used to establish retention time for each hit list compound.

B. Surrogate Compounds

Surrogate organic compounds will be added at a known concentration of 5-25 micrograms per liter to every environmental sample. Surrogate compounds for volatiles analysis and acceptable control limits expressed as percentage of true value are as follows:

Compound	Control Limit
fluorobenzene	81 - 107%
p-bromofluorobenzene	88 - 118%

C. Laboratory Control Standards

Laboratory control standards (LCS) will be employed to identify systematic method and operator errors. The LCS is a mixture of a number of compounds of known concentration in a reference material or spiked into reagent water. They are prepared from EMSL-Cincinnati QC concentrates or standards supplied by the individual laboratory. A minimum of the compounds to be used to make up the LCS for volatile organic analyses is outlined below. There must be one LCS processed through the entire analytical method for each set of samples processed in a group on the same day. Normally, this will be one LCS for every 5 to 15 samples. A control chart should be maintained for each of the compounds with the control limits below (calculated as percent of true value) demonstrating acceptable performance.

TABLE 4-2. INTERNAL QC REQUIREMENTS--VOLATILES IN FOODSTUFFS

Operation check	Frequency	Control limits	Planned corrective action
Calibration of instrument	Daily before analysis of samples	Not applicable	Not applicable
Method blank	Daily before analysis of sample	No significant concentrations found	Check analytical procedure Correct for blank
Calibration check	One mixed standard per 8 hours of analysis	Deviation less than ±20%	
Surrogate compounds	Added to every sample	As specified in text	Check analytical procedure Analyze reference sample Invalidate results
Laboratory control standard (LCS)	One per analysis batch[a]/ analysis day	As specified in text	Check analytical procedure Analyze second reference Invalidate results
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

[a] Analysis batch = group of samples processed as a set, usually containing 15 samples or less.

Compound	Control Limits
Benzene	79 - 107%
Chloroform	90 - 100%
Bromoform	76 - 107%
sym-Tetrachloroethane	67 - 110%
p-Bromofluorobenzene	88 - 118%
Carbon tetrachloride	85 - 102%
Fluorobenzene	81 - 107%
Trichloroethylene	93 - 105%
Tetrachloroethylene	93 - 120%
Chlorobenzene	69 - 107%

D. Method Blanks

One method blank (reagent water) must be processed through the entire analytical procedure for every set of samples processed in a group at the same time on the same day. At least one method blank must be run per work shift. The method blank must not show any signals that correspond to compounds on the Love Canal or priority pollutants lists. If common laboratory contaminants are found in the method blanks, reported values for the same compounds in the environmental samples must be reduced by the amount found in the blank.

E. Replicate Analyses

Intralaboratory precision of the environmental measurements will be evaluated by the measurement of one duplicate (split) of every 10 environmental samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These results must be reported as part of the data base on the Love Canal Study.

4.4 METALS IN HAIR

4.4.1 Analytical Procedures

The analysis of trace elements in hair samples collected from dogs and mice in the Love Canal area is performed using Atomic Absorption Spectroscopy (AAS). The applicability of various AAS techniques to the analysis of individual elements and the appropriate hair cleaning and digestion procedures are detailed below. The elements to be quantified are listed in Table 2-1 (Section 2.1) of this appendix. Note that for hair, the elements of major interest are arsenic, cadmium, and lead.

Either plastic or glass containers are used for samples which will be analyzed for inorganic pollutants only. All sampling containers and labware used are to be acid-cleaned as described in "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020. Hair samples may be stored at ambient temperatures.

A. Hair Cleaning

1. Clean a 1-gram portion of hair[1] by refluxing it in a fume hood for 60 minutes with diethyl ether (purified grade) in a Soxhlet extraction tube equipped with a cellulose thimble (80 x 25 mm), a Friedrichs condenser and a 125-ml flat-bottom flask (Fisher Scientific, Catalog #9-571A, or equivalent).

2. Dry the hair in air to evaporate the ether and then in an oven at 100-105°C.

B. Sample Digestion

1. Weigh the cleaned and dried hair sample to the nearest 1-mg and place in a clean 50-ml beaker.

2. In a hood, add 10-ml of concentrated nitric acid (redistilled grade) to the beaker containing the hair sample.

3. When digest reaction subsides, cover beaker with watch glass and heat the beaker on a hot plate to promote digestion.

4. When reaction appears complete, allow digest to cool. Add another 10-ml concentrated nitric acid and heat the solution (covered by watch glass) at gentle reflux for 10 minutes.

5. Allow digest to cool, add dropwise 2-ml of 30% hydrogen peroxide and warm cautiously to promote reaction.

6. Evaporate solution until approximately 2 ml remain.

7. Transfer the cool digest quantitatively to a 25-ml volumetric flask and rinse the beaker with about 2-ml portions of 0.5% nitric acid. If solids are present in the digest, transfer the solution and the beaker rinsings to the volumetric flask through a Whatman No. 2 filter (or equivalent).

8. Dilute digest in volumetric flask to volume mark with 0.5% nitric acid, stopper flask and invert repeatedly to mix solution.

C. Elemental Analysis

1. For arsenic and lead, analysis is performed using the furnace AAS methods described in "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, reproduced in Section 7.8 of this appendix. These are Method 206.2 for arsenic, which includes addition of nickel, and Method 239.2 for lead.

2. For cadmium analysis, the flame atomic absorption technique described in Method 213.1 in the above EPA manual should provide adequate sensitivity. If necessary, Method 213.2, cadmium by furnace AAS may also be used.

3. For mercury, analysis is to be performed by the cold vapor technique as described in Methods 245.1 or 245.2 of the above EPA manual.

4. For the remaining elements of interest, analysis is to be performed using the furnace AAS method for each element as described in the EPA manual. Furnace AAS was chosen to conserve solution, essential with the limited size of the hair samples, and to provide highest sensitivity.

Reference

1. Anke, M. and Risch, M., "Haaranalyse and Spurenelementstatus," Gustav Fischer, Jena, German Democratic Republic, 1979; Anke, M., Der Mengen-und Spurenelementgehalt des Rinderhaares, Archiv für Tierernährung 17: 461-468, 1965.

4.4.2 Quality Control Procedures

Quality control activities required for the analysis of trace elements in biological materials are described below in some detail. In addition, the standardization and calibration procedures described in the standard analytical methods are to be followed in these analyses. A summary of the type, frequency, control limits and corrective action for these QC activities is given in Table 4-3.

A. Laboratory Control Standards

For all methods, laboratory control standards (LCS) will be employed to monitor systematic method and operator errors. The LCS, generally, is a solution of one or more analytes of known concentration in reagent water which is carried through the entire sample preparation and analysis procedure.

For these analyses, two types of LCS will be used. The first is the trace elements in water standard reference material (SRM 1643a) available from the National Bureau of Standards, Washington, D.C. The certified content of this SRM is given below. The second type of LCS is water spiked with known amounts of the elements of interest. Spiked concentrations should be approximately 4-5 times the analytical detection limit or in the range of the trace elements in water SRM.

SRM 1643a CONTENT

Analyte	Concentration (ng/g)
Arsenic	76 ± 7
Barium	46 ± 2
Beryllium	19 ± 2
Cadmium	10 ± 1
Chromium	17 ± 2
Copper	18 ± 2
Lead	27 ± 2
Mercury*	(<0.2)
Nickel	55 ± 3
Selenium	11 ± 1
Silver	2.8 ± 0.3
Zinc	72 ± 4

One of each type LCS must be processed for approximately every twenty hair samples analyzed. At a minimum, two spikes and two SRM 1643a samples must be analyzed for the full complement of doghair samples and the same number of each for the total number of mousehair samples. A control chart must be maintained for each of the analytes.

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*Mercury is not certified.

TABLE 4-3. INTERNAL QC REQUIREMENTS - METALS IN HAIR

Operation check	Frequency	Control limits	Corrective action planned
Method blank (reagent water)	One for every 20 samples	No significant concentrations found	Correct for blank Check analytical procedure
Laboratory control standard (LCS)	One of each type for every 20 samples	±2 Standard deviations	Check analytical procedure Analyze second reference sample Invalidate results
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

Control limits for each of the analytes have been established at ±2 standard deviations. Any measured value that falls beyond the control limits shall trigger an investigation to determine the cause of the deviation and a correction of the problem. Values of environmental measurements from samples processed during that same work shift must be remeasured or not reported unless a satisfactory justification is prepared.

B. Method Blanks

Method blanks (reagent water) must be processed at a rate of approximately one for every twenty samples. This must at a minimum result in three method blanks for the total number of doghair samples and two for the total mousehair samples. The method blanks must be processed through the entire analytical procedure with the field samples. If common laboratory contaminants are found in the method blanks and it is determined that the same contaminants are present in the field samples, reported values for these analytes must be reduced by the amount found in the blank.

C. Replicate Analyses

If sufficient amounts of sample are available, intralaboratory precision of the environmental measurements will be evaluated by measurement of one duplicate of every ten samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These data must be reported with the laboratory results and will be used by EPA in assessing the overall precision of the data.

4.5 METALS IN VEGETATION

4.5.1 Analytical Procedures

The analysis of metals in vegetation samples collected in the Love Canal area is performed using Inductively Coupled Plasma (ICP) or Atomic Absorption Spectroscopy (AAS) after appropriate sample preparation. The ICP method prescribed for these analyses was published in the Federal Register, Vol. 44, No. 233, December 3, 1979, pp. 69559-69564 and is reproduced in this section from the Environmental Reporter Dec. 7, 1979 Full Text Supplement. The AAS methods to be used for individual metals are those given in "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 and reproduced in Section 7.8 of this appendix.

Sample preparation procedures appropriate to each element of interest are given below. In addition, the applicable analytical techniques, (i.e., ICP, flame AAS, flameless AAS) are specified for the elements. Cited references are also reproduced in this section.

Either plastic or glass containers are used for samples which will be analyzed for inorganic pollutants only. All sampling containers and labware used shall be acid-cleaned as described in EPA-600/4-79-020. Vegetation samples may be stored at room temperature.

A. Analysis of Barium, Beryllium, Cadmium, Copper, Lead, Nickel, Silver, Thallium, and Zinc

Digest 1-gram portions of samples with HNO_3 and $HClO_4$ according to the procedures in Reference 1. Add 5-ml of 2% tartaric acid solution and 10-ml NH_4OH (1:1) solution before silver analysis by atomic absorption.[2] Use this solution for determining the elements listed above by ICP or by using appropriate atomic absorption methods.

B. Analysis of Antimony, Arsenic, Chromium, and Selenium

Digest 1-gram portions of samples with a HNO_3-H_2SO_4-$HClO_4$ mixture and determine antimony, arsenic, and selenium by hydride atomic absorption according to the procedure given in reference 3 or by the appropriate furnace AA methods from reference 1. These are Method 204.2 for antimony, Method 206.2 for arsenic, and Method 270.2 for selenium. Chromium may be analyzed by ICP or AAS.

C. Analysis of Mercury

Digest vegetation samples and measure mercury by AA using the procedures given in reference 4.

References

1. McQuaker, N. R., Brown, D. F., and Kluckner, P. D., Digestion of Environmental Materials for Analysis by Inductively Coupled Plasma-Atomic Emission Spectrometry, Anal. Chem. 51, 1082, 1979.

2. Rooney, R. C., The Determination of Silver in Animal Tissues by a Wet-oxidation Process Followed by Atomic-adsorption Spectrophotometry, Analyst 100, 471, 1975.

3. Fiorino, J. A., Jones, J. W., and Capar, Stephen G., Sequential Determination of Arsenic, Selenium, Antimony, and Tellurium in Foods via Hydride Atomic Absorption Spectrometry, Anal. Chem. 48, 120, 1976.

4. Munns, R. K. and Holland, D. C., Rapid Digestion and Flameless Atomic Absorption Spectroscopy of Mercury in Fish: Collaborative Study, J. Assoc. Off. Anal. Chem. 60, 833, 1977.

The following is an example of the results for samples 2 to 30 of a 30 sample study:

Pollutant (µg/l)		Surrogate standard (µg/l)			
Sample	Found	Added	Found	Percent recovery	
2	14	100	90	90	
3	15	100	89	89	
4	20	90	100	100	
5	11	100	107	107	
6	17	100	100	100	Update recovery for 99.*
7	18	100	100	100	
8	10	100	75	75	Not acceptable, disregard results.
9	14	100	98	98	
10	13	100	93	93	
11	12	100	94	94	Update recovery for 98.**
12	20	100	95	95	
30	15	100	96	96	Give final statistic on recovery of 98.

*Includes 20 results, 12 validation, 3 first day and days 2 through 6. Mean = 99. Std. Dev. = 4.6. Acceptable range 86–113%.
**Includes 25 results; day 8 result not included. Mean = 98. Std. Dev. = 4.6. Acceptable range 84–112%.

Appendix IV.—Inductively Coupled Plasma Optical Emission Spectrometric Method (ICP) for Trace Element Analysis of Water and Wastes

Inductively Coupled Plasma (ICP) Optical Emission Spectrometric Method for Trace Element Analysis of Water and Wastes

Interim

U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268

October 1979.

Foreword

This method has been prepared by the staff of the Environmental Monitoring and Support Laboratory—Cincinnati, with the cooperation of the EPA–ICP Users Group. Their cooperation and support is gratefully acknowledged.

This method represents the current state-of-the-art, but as time progresses, improvements are anticipated. Users are encouraged to identify problems and assist in updating the method by contacting the Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

Inductively Coupled Plasma (ICP) Optical Emission Spectrometric Method for Trace Element Analysis of Water and Wastes

1. Scope and Application.

1.1 This method may be used for the determination of dissolved, suspended, or total elements in surface water, drinking water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken to ensure that potential interference are taken into account when dissolved solids exceed 1500 mg/l. (See 4.2)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps *must* be taken to correct for potential interference effects.

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

Table 1—*Recommended Wavelengths* [1] and Estimated Instrumental Detection Limits

Element	Wavelength, nm	Estimated detection limit, µg/l [2]
Aluminum	308.2	45
Arsenic	193.7	53
Barium	455.4	2
Beryllium	313.0	0.3
Boron	249.8	5
Cadmium	226.5	4
Calcium	317.9	10
Chromium	267.7	7
Cobalt	228.6	7
Copper	324.7	6
Iron	259.9	7
Lead	220.3	42
Lithium	670.7	4
Magnesium	279.1	30
Manganese	257.6	2

Table 1—*Recommended Wavelengths* [1] and Estimated Instrumental Detection Limits—Continued

Element	Wavelength, nm	Estimated detection limit, µg/l [2]
Molybdenum	202.0	8
Nickel	231.6	15
Potassium	766.4	see [3]
Selenium	196.0	75
Silica (SiO$_2$)	288.1	27
Silver	328.0	7
Sodium	588.9	29
Strontium	407.7	0.5
Vanadium	292.4	8
Zinc	213.8	2

[1] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 4.1.1).

[2] The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Optical Emission Spectroscopy Prominent Lines," EPA-600/4-79-017. Detection limits are sample dependent and as the sample matrix varies, these concentration values may also vary.

[3] Highly dependent on operating conditions and plasma position.

2. Summary of Method.

2.1 The method describes a technique for the simultaneous of sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. Additional interferences named in 4.1 should also be recognized and appropriate corrections made.

3. Definitions.

3.1 *Dissolved*—Those elements which will pass through a 0.45 µm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 µm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 8.3), or the sum of the dissolved plus suspended concentrations (Section 8.1 plus 8.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 6.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. funtional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst. Should be included in the analytical scheme with a frequency of 10%. (See 6.6.1.)

3.8 *Reference standard*—A solution obtained from an outside source having known, verified values. Must be used initially to verify the calibration standards and analyzed thereafter as a blind sample on a weekly frequency. (See 6.6.2.)

3.9 *Calibration standards*—A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 6.4.)

3.10 *Linear dynamic range*—The concentration range over which the analytical curve remains linear.

3.11 *Reagent blank*—A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 6.5.2.)

3.12 *Calibration blank*—A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 6.5.1.)

3.13 *Method of standard addition*—The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 9.6.1.)

4. Interferences.

4.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

4.1.1 *Spectral interferences* can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line.

4.1.2 *Physical interferences* are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. (See Note 1.) If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques.

Note 1.—The use of a peristaltic pump may lessen these interferences.

4.1.3 *Chemical interferences* are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

4.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 4.2.1 through 4.2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values.

4.2.1 *Serial dilution*—If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit (13.3) that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

4.2.2 *Spike addition*—The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

Caution.—The standard addition technique does not detect coincident spectral overlap. If suspected, use of an alternate wavelength or comparison with an alternate method is recommended (See 4.2.3).

4.2.3 *Comparison with alternate method of analysis* —When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

4.2.4 *Wavelength scanning of analyte line region*—If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

5. Apparatus.

5.1 Inductively Coupled Plasma (ICP) Optical Emission Spectrometer.

5.1.1 Computer controlled atomic emission spectrometer with background correction.

5.1.2 Radiofrequency generator.

5.1.3 Argon gas supply, welding grade or better.

5.2 Operating conditions—Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument.

6. Reagents and standards.

6.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

6.1.1 *Acetic acid*, conc. (sp gr 1.06).

6.1.2 *Aqua regia:* Mix cautiously 3 parts conc. HCl (sp gr 1.19) and 1 part conc. HNO_3 (sp gr 1.41) just before use.

6.1.3 *Hydrochloric acid*, conc. (sp gr 1.19).

6.1.4 *Hydrochloric acid*, (1+1): Add 500 ml conc. HCl (sp gr 1.19) to 400 ml deionized, distilled water and dilute to 1 liter.

6.1.5 *Nitric acid*, conc. (sp gr 1.41).

6.1.6 *Nitric acid*, (1+1): Add 500 ml conc. HNO_3 (sp gr 1.41) to 400 ml deionized, distilled water and dilute to 1 liter.

6.2 *Deionized, distilled water:* Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water.

6.3 *Standard stock solutions* may be purchased or prepared from ultra high purity grade chemicals or metals

(Caution: See Note 2). All salts must be dried for 1 h at 105° C unless otherwise specified.

Note 2.—Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow:

6.3.1 *Aluminum solution, stock,* 1 ml = 100 μg Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 ml of (1+1) HCl and 1 ml of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 ml of (1+1) HCl and dilute to 1,000 ml with deionized, distilled water.

6.3.2 *Arsenic solution, stock,* 1 ml = 100 μg As: Dissolve 0.1320 g of As_2O_3 in 100 ml of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 ml conc. NHO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.3 *Barium solution, stock,* 1 ml = 100 μg Ba: Dissolve 0.1516 g $BaCl_2$ in 10 ml deionized, distilled water with 1 ml (1+1) HCl. Add 10.0 ml (1+1) HCl and dilute to 1,000 ml with deionized, distilled water.

6.3.4 *Beryllium solution, stock,* 1 ml = 100 μg Be: Dissolve 1.127 g $Be_4O(C_2H_3O_2)_6$, beryllium acetate basic, in a minimum amount of conc. acetic acid. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.5 *Boron solution, stock,* 1 ml = 100 μg B: Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water and dilute to 1,000 ml. Because H_3BO_3 loses weight on drying at 105° C, use a reagent meeting ACS specifications and keep the bottle tightly stoppered to prevent the entrance of atmospheric moisture.

6.3.6 *Cadmium solution, stock,* 1 ml = 100 μg Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.7 *Calcium solution, stock,* 1 ml = 100 μg Ca: Suspend 0.2498 g $CaCO_3$ dried at 180° C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.8 *Chromium solution, stock,* 1 ml = 100 μg Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete, acidify with 10 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.9 *Cobalt solution, stock,* 1 ml = 100 μg Co: Dissolve 0.1407 g Co_2O_3 in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.10 *Copper solution, stock,* 1 ml = 100 μg Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.11 *Iron solution, stock,* 1 ml = 100 μg Fe: Dissolve 0.1430 g Fe_2O_3 in 10 ml deionized, distilled water with 1 ml (1+1) HCl. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.12 *Lead solution, stock,* 1 ml = 100 μg Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.13 *Lithium solution, stock,* 1 ml = 100 μg Li: Dissolve 0.5323 g Li_2CO_3 slowly in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.14 *Magnesium solution, stock,* 1 ml = 100 μg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.15 *Manganese solution, stock,* 1 ml = 100 μg Mn: Dissolve 0.5225 g $Mn(NO_3)_2<6H_2O$ (do not dry) in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.16 *Molybdenum solution, stock,* 1 ml = 100 μg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1,000 ml.

6.3.17 *Nickel solution, stock,* 1 ml = 100 μg Ni: Dissolve 0.4953 g $Ni(NO_3)_2<6H_2O$ in deionized, distilled water. Add 10 ml of conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.18 *Potassium solution, stock,* 1 ml = 100 μg K: Dissolve 0.1907 g KCl, dried at 110° C, in deionized, distilled water dilute to 1,000 ml.

6.3.19 *Selenium solution, stock,* 1 ml = 100 μg Se: Dissolve 0.1727 g H_2SeO_3 in deionized, distilled water and dilute to 1,000 ml.

6.3.20 *Silica solution, stock,* 1 ml = 100 μg SiO_2: *Do not dry.* Dissolve 0.4730 g $Na_2SiO_3<9H_2O$ in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.21 *Silver solution, stock,* 1 ml = 1 μg Ag: Dissolve 0.1575 g $AgNO_3$ in 100 ml of deionized, distilled water and 10 ml conc. HNO_3. Dilute to 1,000 ml with deionized, distilled water.

6.3.22 *Sodium solution, stock,* 1 ml = 100 μg Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.23 *Strontium solution, stock,* 1 ml = 100 μg Sr: Dissolve 0.2416 g $Sr(NO_3)_2$ in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.24 *Vanadium solution, stock,* 1 ml = 100 μg V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.25 *Zinc solution, stock,* 1 ml = 100 μg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.4 *Mixed calibration standard solutions*—Prepared mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 6.4.1 thru 6.4.6) Add 2 ml of (1+1) HNO_3 and 2 ml of (1+1) HCl and dilute to 100 ml with deionized, distilled water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a TFE fluorocarbon bottle for storage. Fresh mixed standards should be prepared weekly. Some typical combinations follow:

6.4.1 *Mixed standard solution I*—Iron, manganese, cadmium, lead, and zinc.

6.4.2 *Mixed standard solution II*—Beryllium, copper, strontium, vanadium, and cobalt.

6.4.3 *Mixed standard solution III*—Molybdenum, silica, lithium, and barium.

6.4.4 *Mixed standard solution IV*—Calcium, magnesium, sodium, and potassium.

6.4.5 *Mixed standard solution V*—Aluminum, arsenic, boron, chromium, nickel, and selenium.

6.4.6 *Mixed standard solution VI*—Silver.

6.5 Two types of blanks are required for the analysis. The calibration blank (3.12) is used in establishing the analytical curve while the reagent blank (3.11) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

6.5.1 *The calibration blank* is prepared by diluting 2 ml of (1+1) HNO_3 and 2 ml of (1+1) HCl to 100 ml with deionized, distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

6.5.2 *The reagent blank* must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

6.6 In addition to the calibration standards, an instrument check standard (3.7) and a reference standard (3.8) are also required for the analyses.

6.6.1 *The instrument check standard* is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. This standard should be included in the analytical scheme with a frequency of 10%.

6.6.2 *The reference standard* should be prepared according to the instructions provided by the supplier. Following initial verification of the calibration standards, analyze weekly.

7. Sample handling and preservation.

7.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether linear polyethylene, polyproplyene or TFE-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order. (See Notes 3 and 4).

Note 3.—*Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.*

Note 4.—If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples those steps may be eliminated from the procedure.

7.2 Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

7.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus is recommended to avoid possible contamination.) Use the first 50–100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 ml of (1+1) acid per liter should be sufficient to preserve the sample.

7.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

7.2.3 For the determinaion of total or total recoverable elements, the sample is acidified with 5 ml conc. HNO_3 per liter (pH 2) as soon as possible, preferably at the time of collection. The sample is not filtered before processing.

8. Sample Preparation.

8.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described in 8.3.

8.2 For the determinaton of suspended elements, transfer the membrane filter containing the insoluble material to a 250-ml Griffin beaker and add 3 ml conc. HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 ml of conc. HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (DO NOT BAKE), cool, add 2 ml of (1+1) HNO_3 and 2 ml HCl (1+1) per 100 ml dilution and warm the beaker gently to dissolve any soluble material. Wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

8.3 For the determination of total elements, choose a measured, volume of the well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 3 ml of conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3 ml portion of conc. HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness and cool the beaker. Add 2 ml of 1+1 HNO_3 and 2 ml of 1+1 HCl per 100 ml of final solution and warm the beaker to dissolve any precipitate or residue resulting from evaporation. Wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. Adjust the volume based on the expected concentrations of elements present. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

Note 5.—If low determinations of boron are critical, quartz glassware should be used.

8.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 1 ml of HNO_3 (1+1) and 2 ml of HCl (1+1) to the sample and heat on a steam bath or hot plate until the volume has been reduced to 15–20 ml making certain the sample does not boil. After this treatment the sample is filtered to remove insoluble material that could clog the nebulizer, and the volume adjusted to 100 ml. The sample is then ready for analysis. Concentrations so determined shall be reported as "total."

9. Procedure.

9.1 Set up instrument with proper operating parameters established in Section 5.2. Instrument must be allowed to stabilize for at least 30 min prior to operations.

9.2 Initiate appropriaate operating configuration of computer.

9.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 6.4. Flush the system with the calibration blank (6.5.1) between each standard. (See note 6.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE 6.—For boron concentrations greater than 500 µg/l extended flush times of 1 to 2 minutes may be required.

9.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 2 percent (or the established control limits). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

9.5 Begin the sample run flushing the system with the calibration blank (6.5.1) between each sample. (See Note 6.) Analyze an instrument check standard (6.6.1) each 10 samples.

9.6 If it has been found that methods of standard addition are required, the following procedure is recommended.

9.6.1 The standard addition technique (13.2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a small volume V_s of a standared analyte solution of concentration c_s. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$C_x = \frac{S_B V_s c_s}{(S_A - S_B)\ V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

10. Calculation.

10.1 Reagent blanks (6.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

10.2 If dilutions were performed, the appropriate factor must be applied to sample values.

10.3 Results should be reported to the nearest µg/l, up to three significant figures, except calcium, magnesium, sodium, and potassium which are reported to the nearest 0.1 mg/l.

11. Quality Control (Instrumental).

11.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow:

11.1.1 Analyze the instrument check standard (6.6.1) made up of all the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within ± 2% of the expected values or within the established control limits, the analysis is out of control.

11.1.2 For the purpose of verifying interelement and/or background correction factors, analyze a second check standard, prepared in the following manner. Select a representative sample which contains minimal concentrations of the elements of interest. Spike this sample with the analytes of interest at or near 100 µg/l. (For effluent samples of expected high concentrations, spike at an appropriate level.) Values should fall within the established control levels of 1.5 times the standard deviation of the mean value of the check standard. If not, repeat the standardization.

11.1.3 A reference standard (6.6.2) from an outside source, but having known concentration values, should be analyzed as a blind sample on a weekly frequency. Values should be within the established quality control limits. If not, prepare new stock standards.

12. *Precision and Accuracy.*

12.1 In an EPA round phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table II lists the true value, the mean reported value and the mean % relative standard deviation.

Table II.—*ICP Precision and Accuracy Data*

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True value µg/l	Mean reported value µg/l	Mean percent RSD	True value µg/l	Mean reported value µg/l	Mean percent RSD	True value µg/l	Mean reported value µg/l	Mean percent RSD
Be	750	733	0.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

Not all elements were analyzed by all laboratories.

13. References.

13.1 Winge, R. K., V. J. Peterson, and V. A. Fassel, "Inductively Coupled Plasma-Optical Emission Spectroscopy: Prominent Lines, EPA-600/4-79-017.

13.2 Winefordner, J. D., "Trace Analysis: Spectroscopic Methods for Elements," *Chemical Analysis*, Vol. 46, pp. 41-42.

13.3 Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019.

13.4 Garbarino, J. R. and Taylor, H. E., "An Inductively-Coupled Plasma Optical Emission Spectrometric Method for Routine Water Quality Testing," Applied Spectroscopy 33, No. 3 (1979).

13.5 "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.

Appendix V—Biological Oxygen Demand, Carbonaceous Method 405.1 (5 Days, 20° C)

Biochemical Oxygen Demand—Method 405.1 (5 Days, 20° C)

STORET No. 00310, Carbonaceous 80082

1. Scope and Application.

1:1 The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirements of municipal and industrial wastewaters. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD tests are used for the development of engineering criteria for the design of wastewater treatment plants.

1.2 The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20° C for a specified time period (often 5 days). The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

1.3 To obtain values for only carbonaceous BOD, the procedure (2.2) for inhibiting the nitrogeneour oxygen demand using 2-chloro-6(trichloromethyl) pyridine should be used.

2. Summary of Method.

2.1 The sampe of waste, or an appropriate dilution, is incubated for 5 days at 20° C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

2.2 Nitrogenous oxygen demand is inhibited by adding approximately 10 mg of 2-chloro-6(trichloromethyl) pyridine to each BOD bottle prior to adding the sample (or diluted sample) for incubation. Results of samples treated with inhibitor are to be reported as Biochemical Oxygen Demand, Carbonaceous, Storet No. 80082.

3. Comments.

3.1 Determination of dissolved oxygen in the BOD test may be made by use of either the Modified Winkler with Full-Bottle Technique or the Probe Method in this manual.

3.2 Additional information relating to oxygen demanding characteristics of wastewaters can be gained by applying the Total Organic Carbon and Chemical Oxygen Demand tests (also found in this manual).

3.3 The use of 60 ml incubation bottles in place of the usual 300 ml incubation bottles, in conjunction with the probe, is often convenient.

4. Precision and Accuracy.

4.1 Eighty-six analysts in fifty-eight laboratories analysed natural water samples plus an exact increment of biodegradable organic compounds. At a mean value of 2.1 and 175 mg/l BOD, the standard deviation was ±0.7 and ± 26 mg/l, respectively (EPA Method Research Study 3).

4.2 There is no acceptable procedure for determining the accuracy of the BOD test.

5. References

5.1 The procedure to be used for this determination is found in: "Standard Methods for the Examination of Water and Wastewater, 14th edition," p. 543, Method 507 (1975).

5.2 Young, J. C., "Chemical Methods for Nitrification Control," J. Water Poll. Control Fed., 45, p. 637 (1973).

507 Oxygen Demand (Biochemical)

1. Discussion

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The test measures the oxygen required for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. It also may measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless oxidation of nitrogenous compounds is prevented by an inhibitor.

The method consists of placing a sample in a full, air-tight bottle and incubating the bottle under specified conditions for a specific time. Dissolved Oxygen (DO) is measured initially and after incubation. The difference in DO is the oxygen used and from it the BOD can be computed.

The bottle size, incubation temperature, and incubation period are all specified. Because most wastewaters contain more oxygen-demanding materials than the quantity of DO in oxygen-saturated water, it is necessary to dilute the sample before incubation to bring the oxygen required and oxygen supply into appropriate balance. Because bacterial growth requires such nutrients as nitrogen, phosphorus, and trace metals, these are added to the dilution water which is buffered to ensure that the pH of the incubated bottle remains in a range suitable for bacterial growth. Complete stabilization of a sample may require a period of incubation too long for practical purposes; therefore, the 5-day period has been accepted as standard.

Measurements of BOD that include both carbonaceous oxygen demand and nitrogenous oxygen demand generally are not useful; therefore, where appropriate, may be an inhibiting chemical used to prevent nitrogenous oxidation. Carbonaceous and nitrogenous demands are measured separately for predicting oxygen suppression in receiving streams and oxygen requirements for treatment plant design and operation.

The inclusion of ammonia in the citation water demonstrates that there is no intent to include the oxygen demand of reduced forms of nitrogen in the BOD test. If this ammonia were oxidized, errors would result because the oxygen use would not be due exclusively to pollutants in the sample.

The extent of oxidation of nitrogenous compounds during the 5-day incubation period depends on the presence of micro-organisms capable of carrying out this oxidation. Such organisms usually are not present in raw sewage or primary effluent in sufficient numbers to oxidize significant quantities of reduced nitrogen forms in the 5-day BOD test. Currently any biological treatment plant effluents contain a significant population of nitrifying organisms. Consequently, oxidation of nitrogenous compounds can occur within such samples and inhibition of nitrification is recommended for all samples of secondary effluent, for samples seeded with secondary effluent, and for samples of polluted waters.

Samples for BOD analysis may undergo significant degradation during storage between collection and analysis. This results in a low BOD value. Minimize reduction of BOD by promptly analyzing the sample or by cooling it to

AIDS FOR ANALYTICAL CHEMISTS

Digestion of Environmental Materials for Analysis by Inductively Coupled Plasma–Atomic Emission Spectrometry

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Recently various workers have reported on the use of an inductively coupled plasma–atomic emission spectrometer (ICP/AES) for the simultaneous multielement analysis of a variety of environmental materials. These materials have included waters (*1, 2*), soils (*3*), airborne particulates (*4*), and biological tissues (*5–7*). In ICP/AES analyses, the digested or extracted sample is presented as a liquid, and the nebulizer used for sample transport places certain restraints on the sample, i.e., the glass construction of the nebulizer precludes the presence of hydrofluoric acid in the digests and, in order to avoid errors introduced by fluctuations in nebulizer performance, variations in the acid content of samples (and standards) must be minimized (*5, 8, 9*).

Only limited information on digestion procedures compatible with ICP/AES work is available. For example, a procedure for tissue samples which yields a residual acid content of 17% $HClO_4$ and a procedure for rock samples which yields a residual acid content of 3% $HClO_4$/20% HCl have been described (*3, 5*). However, a comprehensive approach producing equivalent acid contents and applicable to a variety of sample types has evidently not appeared.

In the present work such an approach is discussed. Both $HNO_3/HClO_4$ and $HNO_3/HF/HClO_4$ digestion procedures are described. The procedures are variously applicable to waters, soils, tissues, and airborne particulates and provide for a mean residual perchloric acid content of 3.5% in the prepared digests. Data defining observed fluctuation about this mean value of 3.5% are presented and the implications of sample acid content on analytical accuracy are discussed. The implications of digestion efficiencies on analytical accuracy are also discussed.

EXPERIMENTAL

Reagents and Apparatus. The acids used were reagent grade HNO_3 (65%), HF (42%), and $HClO_4$ (72%). All digestions were carried out in open 150-mL beakers using a hot plate in a perchloric acid fume cupboard. The surface temperature of the hot plate was held at 250 °C for all digestion procedures. All beakers used, whether Pyrex or Teflon, were of uniform shape.

Digestion Procedures. The procedures used for the various materials follow. Note that in all cases once the digests are taken to dense white fumes of $HClO_4$ they are removed from the hot plate, cooled, diluted to 100 mL, and then filtered using Whatman No. 42 paper. Usually the fuming step is accompanied by the digest going to a lighter color and the digests are removed when this color change is complete.

Water Samples. A representative 100-mL sample is evaporated to about 5 mL in the presence of 5 mL HNO_3; an additional 5 mL HNO_3 is added and the sample is taken to near dryness; 5.5 mL $HClO_4$ is then added and the sample digested until dense white fumes of $HClO_4$ appear.

Soil Samples. Soils are homogenized and ground so as to pass a 100-mesh sieve. A 1.0-g sample in the presence of 10 mL HNO_3 is then taken to near dryness; 5.5 mL $HClO_4$ is then added and the sample digested until dense white fumes of $HClO_4$ appear. When a total analysis is required, a 0.5-g sample and Teflon

Table I. Acid Content of Digested Samples: Replicates of the Same Samples

sample[a]	no. of replicates	acid content, %
water	7	3.57 ± 0.09
particulate	7	3.60 ± 0.07
tissue	7	3.33 ± 0.11
soil	7	3.45 ± 0.10
tissue*	7	3.48 ± 0.12
soil*	7	3.51 ± 0.09

[a] An asterisk * identifies a $HF/HNO_3/HClO_4$ procedure. All other samples were carried through the $HNO_3/HClO_4$ procedure.

Table II. Acid (and Salt) Content of Digested Samples: Replicates of Different Samples of the Same Sample Type

sample type[a]	no. of samples	acid content, %	salt content, %[b]
water	10	3.59 ± 0.14	0.03 ± 0.007
particulate	10	3.58 ± 0.22	0.02 ± 0.005
tissue	10	3.44 ± 0.26	0.44 ± 0.09
soil	10	3.51 ± 0.21	0.48 ± 0.19
tissue *	10	3.46 ± 0.23	0.43 ± 0.07
soil *	10	3.51 ± 0.15	0.42 ± 0.17
composite result	60	3.5 ± 0.3,	

[a] An asterisk * identifies a $HF/HNO_3/HClO_4$ digestion procedure. All other samples were carried through the $HNO_3/HClO_4$ procedure. [b] Percent salt content is based on the presence of Al, Fe, Ca, Mg, Na, K, and NH_4 as phosphates, sulfates, and perchlorates. (Chlorides and nitrates are not present because of volatilization as HCl and HNO_3 during the digestion step.)

beakers are used. The $HNO_3/HF/HClO_4$ procedure parallels the $HNO_3/HClO_4$ procedures except that after the treatment with HNO_3 the sample is taken to dryness in the presence of 5.0 mL HF.

Tissue Samples. Tissues (plant or animal) are homogenized (*10*) and a 1.0-g sample is then digested in the presence of successive 15- and 10-mL aliquots of HNO_3; after each addition the sample is taken to near dryness; next, 5.5 mL $HClO_4$ is added and the sample digested until dense white fumes of $HClO_4$ appear. When a total analysis is required, 1.0-g samples and Teflon beakers are used. The $HNO_3/HF/HClO_4$ procedure parallels the $HNO_3/HClO_4$ procedure except that after the treatment with HNO_3 the sample is taken to dryness in the presence of 5.0 mL HF.

Particulate Samples. Two 46-mm diameter disks, representing 8.12% of the exposed filter area, are digested in the presence of 10 mL HNO_3; next, 5.5 mL $HClO_4$ is added and the sample digested until dense white fumes of $HClO_4$ appear. Note that high volume samplers are used to collect the airborne particulates (*11*). The sampling rate and sampling duration are normally 40 ft³/min and 24 h, respectively.

RESULTS AND DISCUSSION

Digest Acid Content. The addition of the $HClO_4$ to the samples subsequent to the HNO_3 and/or HNO_3/HF will minimize the amount of $HClO_4$ consumed in oxidizing any residual organic materials, and it was hoped that for all samples an equivalent amount of $HClO_4$ would remain after bringing the digests to fumes of $HClO_4$, thus satisfying the requirements of ICP/AES analysis. Also, during this step all residual HNO_3 and HF could be volatilized, thus providing for a residual acid matrix consisting of $HClO_4$. In order to check the mean $HClO_4$ content of the samples and to define the fluctuations about the mean, a number of samples were analyzed for total acid content (by titration with standard base). Table I indicates that the digestion procedure controls the residual acid content to ±0.1% $HClO_4$. When variations introduced by dissimilarities between samples within a group are introduced (Table II), a standard deviation of between 0.15% and 0.25% $HClO_4$ results. Table II also indicates that, regardless of sample type, the residual acid content of any digest can be expected to be 3.5 ± 0.4% $HClO_4$.

ICP/AES data appearing elsewhere (*9*) indicate that when the standards are prepared in 3.5% $HClO_4$ this fluctuation of up to ±0.4% about a mean acid content of 3.5% $HClO_4$ may introduce analytical error of up to ±1.3%. Such a degradation in accuracy is small and we may conclude that the digestion procedures allow for adequate control over the residual acid content of the samples and in so doing are compatible with ICP/AES techniques. Note that variation in total salt content can also produce the same effect as variation in acid content. Since the ability of ICP/AES analytical systems to handle dissolved salts may be limited, the total salt content of standards and samples should be kept below 0.5% (*9*). This criterion for typical sample digests is satisfied (see Table II) and the low salt content together with the fact that $HClO_4$ is the major matrix component will minimize any analytical deviation.

Digestion Efficiency. The acid digestion procedure must not only be compatible with ICP/AES techniques but must also provide for satisfactory extraction efficiencies. Previous workers have described the relative merit of $HNO_3/HClO_4$ digestion procedures in detail (*12, 13*). For most environmental work, a $HNO_3/HClO_4$ digestion is considered adequate since it will typically recover all materials of anthropogenic

Table III. Analytical Results (μg/g): Biological Samples

	SRM 1571 Orchard Leaves				SRM 1577 Bovine Liver			
element	NBS[a]	AES[b]	RSD, %	rec, %	NBS[a]	AES[b]	RSD, %	rec, %
As	10 ± 2	11		110				
Ba	(44)	42 ± 2	4.8	95				
Ca	20 900 ± 300	19 800 ± 500	2.5	95	(123)	127 ± 12	0.4	103
Cr	2.6	2						
Cu	12 ± 1	11 ± 1	9.1	92	193 ± 10	186 ± 2	0.8	96
Fe	300 ± 20	267 ± 6	2.2	89	270 ± 20	244 ± 2	0.8	90
Mg	6 200 ± 200	5 700 ± 60	1.1	92	(605)	573 ± 4	0.7	95
Mn	91 ± 4	86 ± 1	1.2	95	10.3 ± 1.0	10 ± 1	10.0	97
Mo					(3.2)	2		
P	2 100 ± 100	1 900 ± 40	2.1	90				
Pb	45 ± 3	42 ± 1	2.4	93				
Sr	37 ± 1	37 ± 1	2.7	100				
Zn	25 ± 3	26 ± 1	3.8	104%	130 ± 10	131 ± 1	0.7	101
			mean 3.2%	96%			mean 3.7%	97%

[a] Results in parentheses are not certified. [b] Results for 7 replicate samples.

Table IV. **Analytical Results ($\mu g/g$): Soils**

element	ELR-007				ELR-008			
	ELR[a]	AES[b]	RSD, %	rec, %	ELR[a]	AES[b]	RSD, %	rec, %
Al	63 700 ± 1 700	44 600 ± 2 900	6.5	70	66 500 ± 3 700	47 900 ± 3 400	7.1	72
Cd	20 ± 1	19 ± 1	5.3	95				
Cu	95 ± 6	91 ± 3	3.3	96	40 ± 1	36 ± 2	5.7	90
Fe	25 500 ± 100	23 300 ± 200	0.8	91	26 600 ± 300	23 500 ± 300	1.3	88
Mg	5 700 ± 2 170	5 990 ± 220	3.7	105	7 770 ± 2 080	7 160 ± 350	4.9	92
Mn	593 ± 13	449 ± 8	1.8	76	723 ± 15	615 ± 7	1.1	85
P	1 730 ± 250	1 570 ± 60	3.8	91	1 550 ± 60	1 630 ± 40	2.5	105
Pb	1 650 ± 60	1 520 ± 30	2.0	92	275 ± 96	295 ± 28	9.5	107
Zn	2 510 ± 70	2 500 ± 40	1.6	100	208 ± 10	208 ± 13	6.3	100
K	23 900 ± 800	21 500 ± 600	2.8	90	23 400 ± 1 300	22 900 ± 100	0.4	98
			mean 3.2%	91%			mean 4.3%	93%

[a] Uncertified reference values (*16*). [b] Results of 7 replicate samples.

origin (*12*). This is reflected in the fact that regulatory agencies typically do not specify drastic recovery procedures involving HF in defining standards or guidelines for the total metal content of waters and airborne particulates (*10*, *14*, *15*). However, there may be situations (particularly in soil and tissue analysis) where a total analysis is indicated. In these cases HF may be used to release materials associated with the silicate matrix (*15*).

All the digestion procedures described in this work are characterized by a predigestion with HNO_3. The amount of HNO_3 used has been individually adjusted to accommodate the destruction of maximum levels of organic materials in the samples. If destruction of the silicate matrix is required, this is accomplished by subsequent digestion in the presence of HF. Finally, all samples are carried through a perchloric acid digestion. Here the sample is exposed to both a powerful oxidizing system and a source of chloride ions, which aid in the dissolution of many metals.

Selected reference materials were used to check the effectiveness of these digestion procedures. In the case of the tissue samples, standard reference materials (SRM) provided by the National Bureau of Standards were used. These were SRM 1571 Orchard Leaves and SRM 1577 Bovine Liver. In the case of soils, two reference materials used in quality control procedures within this laboratory were used. These were ELR 007 and ELR 008. Characterization of the reference soil materials was achieved by atomic absorption spectrometry (AAS) preceded by dissolution in a $HF/HNO_3/HClO_4$ acid mixture using a pressure vessel (*13*). A description of these materials appears elsewhere (*16*).

Tables III and IV compare reference values for the soil and tissue samples with those obtained using ICP/AES analytical procedures described in another publication (*9*). Note that soil reference values for Ca and Na do not appear because of reagent contamination from boric acid which is used to dissolve the precipitated metal fluorides (*12*, *16*). Reference to the tables indicates that in general the results obtained using the $HF/HNO_3/HClO_4$ digestion procedure of this work compare favorably with the reference values. Some significantly low recoveries (<90%) do appear however. These include Fe recoveries for the tissue samples and Al, Mn, and Fe recoveries for the soil samples. However, when the samples were spiked with the elements in question, quantitative recoveries were obtained. This indicates that the low recoveries noted are not due to digest matrix effects but rather to extraction inefficiencies associated with digestion in open beakers as opposed to a pressure vessel (*12*, *17*) or refluxing apparatus (*5*, *18*).

Precision and Accuracy. The precision and accuracy of an analytical result will be related to both sample preparation and analytical performance. In the case of ICP/AES analysis, the sample preparation considerations must include the effects of acid content together with the usual implications that sample homogeneity and digestion efficiency have for analytical precision and accuracy; i.e., the accuracy will be affected by any deviations in the mean acid content from 3.5% $HClO_4$ and fluctuations about the mean will affect precision. Precision and accuracy results obtained for the reference materials are summarized in Tables III and IV. The mean precision values (as percent relative standard deviations) were 3.2, 3.7, 3.2, and 4.3% for SRM 1571, SRM 1577, ELR 007, and ELR 008, respectively. The corresponding mean recovery values were 96, 97, 91, and 93%. These data indicate acceptable precision and acceptable accuracy (with the exception of low Al, Mn, and Fe recoveries due to digestion inefficiencies).

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The Determination of Silver in Animal Tissues by a Wet-oxidation Process Followed by Atomic-absorption Spectrophotometry

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Silver in animal tissues can be determined at fairly low levels by conventional atomic-absorption spectrophotometry, following wet oxidation. The wet-oxidation stage is difficult when large samples are to be analysed and the final solution must be adjusted in order to minimise losses of silver by adsorption or precipitation. The method has been applied to samples of urine, faeces, individual organs, skin and whole-animal homogenates.

There is little information in the literature on the normal levels of silver in animal tissues or on its toxicity. Thus, the work described below was undertaken as part of a toxicological study involving silver taken orally. The experimental animals included mice, rats and monkeys, and the distribution of the silver in the body was studied.

Atomic-absorption spectrophotometry was the technique chosen for this work; the detection limit is good, less than 0·01 μg ml^{-1}, and because interferences are few, sample preparation is fairly simple.

Experimental

The samples to be analysed varied widely in nature and in mass. They included faeces, urine soaked into filter-paper, individual organs from mice, such as liver, kidney or gut, whole-mouse homogenates, whole-rat homogenates and pieces of monkey skin with varying amounts of subcutaneous fat.

Samples were wet oxidised by a method similar to that described by Nangniot,[1] in which the sample is heated gently with a 1 + 1 mixture of nitric and perchloric acids, using about 5 ml of the acid mixture per gram of organic material present.

The smaller samples, containing up to 2–3 g of organic material, responded well to the method, oxidising smoothly and rapidly to give clear solutions and small white final residues. Recoveries of silver added to portions of rat homogenate tended to be low (see Table I) and this was ascribed to the formation of chloride during the final stages of oxidation. The silver was added to the sample as silver nitrate solution before the addition of the acid mixture. The addition of ammonia solution to the final solutions gave quantitative recoveries within the limits of experimental error, *i.e.*, ±3 per cent. over the range 1–100 μg of silver (Table I).

TABLE I

RECOVERY OF ADDED SILVER

Additions were made to a rat homogenate sample that was prepared from an animal that had not been dosed with silver.

Sample size/g	Procedure	Silver added/μg	Silver found/μg
0·2	HNO_3 - $HClO_4$	1·0	0·54, 0·63
0·2	HNO_3 - $HClO_4$	10	8·6, 7·5
0·2	HNO_3 - $HClO_4$	100	95, 92
0·2	HNO_3 - $HClO_4$ - NH_4OH	1·0	0·98, 1·03
0·2	HNO_3 - $HClO_4$ - NH_4OH	Nil	<0·1, <0·1
0·2	HNO_3 - $HClO_4$ - NH_4OH	10	9·9, 10·4
0·2	HNO_3 - $HClO_4$ - NH_4OH	100	102, 98
10	HNO_3 - $HClO_4$ - NH_4OH	1·0	0·96, 0·99
10	HNO_3 - $HClO_4$ - NH_4OH	100	96, 99
10	HNO_3 - H_2SO_4	100	65, 56
10	HNO_3 - H_2SO_4 - NH_4OH	100	72, 68
10	HNO_3 - $HClO_4$ - NH_4OH	Nil	1·0, 0·95
50	HNO_3 - $HClO_4$ - KCN	Nil	4, 7, 5

Oxidation of whole-mouse homogenates and monkey skin samples caused more difficulty because of the larger amount of organic material present, *i.e.*, up to 10 g, and the relatively high fat content. This procedure relies for safety on the formation of a homogeneous solution, which is not obtained with high-fat materials. Fat usually separates and forms a separate upper phase, so that it reacts only to a limited extent with the nitric acid and remains relatively inert until the situation arises in which a fat - hot perchloric acid interface exists; this situation is hazardous. When such an interface occurred the solutions blackened and began a vigorous ebullition as the last traces of nitric acid boiled off. This necessitated continuous supervision of the oxidation and the addition of further nitric acid as this stage began, which was considered potentially hazardous; alternative methods of oxidation were therefore investigated.

Oxidation mixtures that involved the use of sulphuric acid were found to be unacceptable, as copious amounts of calcium sulphate were deposited at the final evaporation stage and large losses of silver by adsorption were incurred (Table I). Dry ashing was rejected because of the large amounts of objectionable fumes evolved and because the residues obtained were difficult to dissolve. The nitric acid - perchloric acid digestion was therefore retained, despite being recognised as hazardous, as with reasonable care it gave acceptable results.

Whole-rat homogenates caused considerable difficulties in that the animals as supplied were not particularly well homogenised and it appears to be difficult to homogenise effectively an animal of this size. It was agreed with a toxicologist that at least 10 per cent. of the whole body mass would have to be taken in order to ensure a representative sample, and as a male rat weighs up to 600 g, sample masses of 50–100 g were necessary. This range usually corresponded to 150–300 g of homogenate.

Initial attempts to use the nitric acid - perchloric acid oxidation were obviously extremely dangerous, although we have had considerable experience in the wet oxidation of many types of organic material. Five grams of organic matter have usually been regarded as a desirable upper limit and we have never experienced an actual explosion from mixtures of organic matter and perchloric acid. The worst uncontrolled reaction to date has been spontaneous ignition in a beaker, when a reaction mixture had been allowed to blacken and boil to dryness. When using the large, high-fat rat samples it soon became apparent that there was a real danger of an explosion involving tens of grams of material, and a new approach was obviously essential.

Many animal tissues can be dissolved in hot, concentrated nitric acid to give true solutions, and even fat can be distributed by swirling or shaking the vessel to give a relatively homogeneous suspension. If such a solution is added to a large excess of hot perchloric acid in small portions, the organic material will be rapidly oxidised without bringing large amounts of it into contact with perchloric acid. Such a procedure is hazardous in that it requires the handling and transfer of fairly large volumes of hot, concentrated acids, but is much safer from the point of view of risk of explosion.

The procedure given below describes this approach; it should be carried out by an experienced analyst, aware of the dangers, and wearing suitable protective clothing. Gloves and safety glasses are a minimum requirement and all beakers should be handled with tongs. It is very important that the perchloric acid should be boiling, not merely fuming, and that it should be brought back to the boil after each addition of the nitric acid solution and before the next. It is easy to mistake the ebullition of reaction for boiling and if too much organic material is introduced at once, the perchloric acid solution will boil over as a vigorous oxidation takes place.

The solutions obtained from the large rat samples did not respond well to treatment with ammonia solution in order to dissolve the silver chloride. Too much calcium phosphate was present to permit working with final volumes smaller than 500 ml and there was a considerable loss of silver by entrainment (Table I). The use of acidic solutions in order to maintain calcium salts in solution also caused a loss of silver, however, so that it was finally decided to use a cyanide complex, which is soluble and resistant to hydrolysis by dilute acids. There is usually sufficient iron present to complex any excess of cyanide, so that there is little hazard in acidifying the cyanide solution. Recoveries of added silver were found to be good by this method, and the results are given in Table I.

Three procedures are described, for various sample sizes; the smallest sample size compatible with the provision of a representative sample should be used. The results obtained with all three methods are given in Table II.

TABLE II
TYPICAL RESULTS ON TISSUE SAMPLES

Whole-mouse homogenates—

	Total silver/μg
Control	<1
Control	<1

Whole-mouse homogenates and corresponding excreta (all body masses were 20 ± 2 g)—

Silver in whole body, 24 h after dosing/μg	Silver content of faeces in 24 h/μg	Silver content of urine in 24 h/μg
11	10	2·8
5·8	2·4	1·0
12	6·8	3·3
29	5·6	0·9
22	0·4	1·3
36	4·2	2·4

Individual organs—

Time after dosing	Silver in gut/μg	Silver in liver/μg	Silver in kidney/μg
8 h	7·4	1·2	17
48 h	2·0	3·8	24
72 h	3·4	8·2	0·8
7 d	1·4	1·8	0·8

Monkey skin samples—

Monkey	Sample site	Silver/μg	Silver/μg g⁻¹
M1	Chest	3·6	0·5
	Hand	0·6	0·3
	Foot	4·0	1·0
	Muzzle	18	4·7
M2	Chest	1·6	0·2
	Hand	0·6	0·2
	Foot	1·0	0·2
	Muzzle	0·6	0·1
M3	Chest	2·7	0·4
	Hand	4·4	1·6
	Foot	1·2	0·5
	Muzzle	0·8	0·2

Rat homogenates—

Animal	Body mass/g (10–20% taken)	Silver in whole body/μg
1	425	3280
2	515	4710
3	259	21
4	556	125
5	256	5080
6	287	60
7	245	880
8	245	4000

Method

Reagents

Nitric acid, sp. gr. 1·42.

Perchloric acid, sp. gr. 1·54.

Nitric acid (1 + 1). Mix equal volumes of nitric acid (sp. gr. 1·42) and water.

Ammonia solution (1 + 1). Mix equal volumes of ammonia solution (sp. gr. 0·89) and water.

Potassium cyanide solution, 1 *per cent.* Dissolve 10 g in water and dilute to 1 l.

Tartaric acid solution, 2 *per cent.* Dissolve 20 g in water and dilute to 1 l.

Procedure 1. Tissue Samples up to 0·5 g (*e.g.*, Individual Organs)

Weigh the sample into a 150-ml squat beaker and add 5 ml each of concentrated nitric and perchloric acids. Cover the beaker and evaporate the contents on a hot-plate at a rate such that the nitric acid is boiled off in 10–15 min and the perchloric acid begins to fume. If the solution darkens at this stage add a few drops of nitric acid in order to clear it. When oxidation has ceased, and the solution is colourless, remove the cover and evaporate the solution to dryness.

Re-dissolve the residue in 2 ml of nitric acid (1 + 1), cool and transfer it to a 25-ml calibrated flask. Add 2 ml of 2 per cent. tartaric acid solution, rinse the beaker with 5 ml of ammonia solution (1 + 1), add the rinsings to the flask and dilute to volume with water.

Determine the amount of silver in this solution by use of atomic-absorption spectrophotometry, using the 328·0-nm resonance line for highest sensitivity; a stoicheiometric air-acetylene flame has been found to give the best results in our laboratory. Standardise the instrument against aqueous silver solutions containing the same concentrations of ammonia and nitric acid.

Procedure 2. Tissue Samples up to 10 g (*e.g.*, Whole Mice)

Weigh the sample into a 600-ml squat beaker and add 30 ml of concentrated nitric acid. Cover the beaker. Boil the mixture gently until the initial reaction and effervescence has subsided, then evaporate it to as small a volume as possible without allowing the solution to boil dry. Add 30 ml of concentrated nitric acid and 30 ml of perchloric acid and evaporate again until incipient fumes of perchloric acid appear. At this stage the solution will probably darken; if darkening occurs, add 1–2 ml of nitric acid to the fuming solution. A vigorous ebullition will occur and as the nitric acid boils off the solution will darken again; the addition of nitric acid should then be repeated. Continue with this procedure until the solution does not darken beyond a clear brown colour; at this stage there must be at least 10 ml of perchloric acid still present, and more should be added if necessary. Make the same additions of extra acids to the blank determination and continue to evaporate to fumes until the solution is colourless or very pale yellow. Remove the cover from the beaker and evaporate the solution to dryness.

Re-dissolve the residue in 5 ml of nitric acid (1 + 1), cool the solution and transfer it to a 50-ml calibrated flask. Add 5 ml of 2 per cent. tartaric acid solution, rinse the beaker with 10 ml of ammonia solution (1 + 1) and add the rinsings to the flask. Make the solution up to volume and determine the silver as in Procedure 1.

Procedure 3. Tissue Samples in Excess of 10 g

Weigh the frozen homogenate and cut portions corresponding to 10–20 per cent. of the homogenate; an amount of sample corresponding to 50–60 g of the animal is the most that can be handled. As many animals cannot easily be homogenised, as large a sample as possible should be taken in order to ensure that it is representative.

Transfer the sample to a 600- or 800-ml squat beaker, add 100 ml of concentrated nitric acid and heat. Reduce the level of heating as necessary if frothing becomes excessive; it may be necessary in extreme cases to use surface heating with an infrared lamp. When the volume has been reduced to about 20 ml, monitor the evaporation continuously and remove the beaker from the heat as soon as the residue begins to darken. Then add 100 ml of concentrated nitric acid and heat the mixture to boiling.

Heat 120 ml of perchloric acid (sp. gr. 1·54) to boiling in a 600- or 800-ml conical flask. Swirl the solution in nitric acid to disperse the fat throughout, and cautiously pour a few millilitres into the boiling perchloric acid. A violent ebullition will take place, and the solution may darken. If the solution darkens appreciably, add a further 50 ml of nitric acid to the squat beaker in order to dilute the organic matter further. Allow the oxidation to reach completion and the solution to clear, and add a further few millilitres of nitric acid solution. Care should be taken that only a few millilitres are added at a time, or the oxidation may become uncontrolled. When all of the solution has been transferred and the final oxidation completed, allow the perchloric acid to cool. Then, add 20 ml of nitric acid to the beaker, transfer the solution in perchloric acid to it and evaporate the whole solution first to fumes of perchloric acid and finally to dryness.

Re-dissolve the residue in 5 ml of nitric acid (1 + 1), and transfer the solution to a 100-ml calibrated flask. Rinse the beaker with water, then with 10 ml of ammonia solution (1 + 1), and add the rinsings to the flask. At this stage calcium phosphate and metal hydroxides will precipitate. Next rinse the beaker with 10 ml of 1 per cent. potassium cyanide solution and again add the rinsings to the flask, and then add 1 + 1 nitric acid dropwise until the precipitate just re-dissolves. Finally, cool the solution, dilute it to 100 ml with water and determine the silver as in Procedure 1.

Discussion

The recoveries of added silver suggest that the method is accurate to about the same degree as the reproducibility, *i.e.*, 10–15 per cent. relative at the blank level, which is usually less than 10 μg of silver with the volumes of reagents required for 50 g of sample. The detection limit is set by the variance of the blank, and is about 0·1 $\mu g\ g^{-1}$ of sample.

The interpretation of the results has more toxicological than analytical significance. It can be seen that the level of silver in unexposed animals is less than 0·1 $\mu g\ g^{-1}$, and that large amounts of silver are absorbed into the tissues following ingestion.

The number of distribution and elimination experiments was small, but it can be seen that in mice a large proportion of the silver is eliminated in the faeces. It also passes fairly rapidly from the gut to the kidneys, where a further substantial fraction is lost via the urine; there is some evidence of retention in the liver for a period of a few days.

The distribution experiments on monkeys were inconclusive, which may be a result of the difficulty of removing skin samples with a constant amount of subcutaneous fat, or it may be caused by the small number of animals involved.

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Sequential Determination of Arsenic, Selenium, Antimony, and Tellurium in Foods via Rapid Hydride Evolution and Atomic Absorption Spectrometry

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Analysis of acid digests of foods for As, Se, Sb, and Te has been semiautomated. Hydrides generated by controlled addition of base stabilized NaBH$_4$ solution to acid digests are transported directly into a shielded, hydrogen (nitrogen diluted), entrained-air flame for atomic absorption spectrophotometric determination of the individual elements. The detection limits, based on 1 g of digested sample, are approximately 10 to 20 ng/g for all four elements. Measurement precision is 1–2% relative standard deviation for each element measured at 0.10 µg. A comparison is made of results of analysis of lyophilized fish tissues for As and Se by instrumental neutron activation (INAA), hydride generation with atomic absorption spectrometry, fluorometry, and spectrophotometry. NBS standard reference materials (orchard leaves and bovine liver) analyzed for As, Se, and Sb by this method show excellent agreement with certified values and with independent NAA values.

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Arsenic, selenium, antimony, and tellurium have traditionally been rather difficult elements to determine. Most analyses for these elements have been performed using absorption spectrophotometry or fluorometry (*1, 2*). However, these classical techniques have gradually yielded to the operationally simpler atomic absorption spectrometry (AAS). Because of inadequate detection capability for these elements, AAS has been used in conjunction with separation and/or concentration techniques (*3*). As a means of both separation and concentration, the formation of the gaseous hydrides has many advantages, especially for AAS determinations. Minimization of interferences and possible utilization of the highly transparent hydrogen diffusion flame are two obvious advantages of hydride volatilization (*4, 5*). Generally, the hydrides are formed either by the reductive action of granular zinc in acid media (*6–9*) or, more recently, by reaction of the analyte(s) in acid media with sodium borohydride either as uniform pellets or in aqueous solution (*10–12*). Evolution and transport of the hydrides from the acid medium are governed by a number of parameters among which are the chemical nature, form, and concentration of the reductant, acid concentration, and carrier gas flow rate.

With zinc or $NaBH_4$ pellets as the reductant, it is common practice to collect the hydrides in a purgeable reservoir (e.g., a balloon) subsequent to venting them to the flame of an atomic absorption spectrophotometer. The precision of the measurements is very dependent upon the skill of the analyst since most operations involved (dosing stopcocks, injection of zinc slurries, manipulation of valves, etc.) are manual.

Schmidt et al. (*13*) and Kan (*14*) have described automated methods based on the evolution of hydrides using aqueous $NaBH_4$ reductant. These works demonstrate the excellent precision and detection capabilities obtainable, as well as the analytical speed afforded by automated chemical procedures. Both of these automated methods employ peristaltic pumping systems to provide continuous mixing of the reactants, and result is a steady-state signal. The instrument described in this paper is a semi-automatic hydride generator in which a $NaBH_4$/NaOH solution is metered into a reaction vessel containing an acid-oxidized food sample. The hydrides are produced quantitatively and are carried directly into a shielded, nitrogen-diluted, hydrogen diffusion flame by the flow of hydrogen produced by the $NaBH_4 + H_3O^+$ reaction. Under these conditions, a transient (peak) signal is produced rather than a steady-state signal. The apparatus is considerably simpler and less expensive than those based on peristaltic pumping systems and is capable of comparable precision, accuracy, speed, and detection limits.

EXPERIMENTAL

Apparatus. The hydride generator (Figure 1) consists of: (1) a unique reaction head constructed of acrylic plastic which incorporates two Teflon metering valves, a vent tube, and a tapered, rubber sheathed stopper for connection of an 8-inch, heavy-wall test tube reaction cell; (2) a 4-cam, 90-sec/rev motor driven timer; (3) two Teflon-bodied, relay-actuated solenoid valves; (4) a large diaphragm, single stage, low-pressure gas regulator; and (5) two 1-l. reagent reservoirs. (Details of construction are available upon request.)

A Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer equipped with a 3-slot, 10-cm Boling-type burner head was used for most of the work reported in this article. However, different atomic absorption instruments were used satisfactorily by other laboratories involved in testing the hydride generator. Both single element hollow cathode lamps (HCL) and electrodeless discharge lamps (EDL) were used as the primary atomic line sources. The extremely "soft" diffusion flame was protected from room air currents by a burner shield equipped with quartz end windows and Pyrex side plates (Figure 2). Use of the burner shield improved precision approximately twofold. The gaseous reaction products from the generator were delivered to the burner via Latex rubber tubing and into the burner mixing chamber by replacement of the nebulizer with a simple straight-through glass adapter, identical to one described by Dalton and Malanoski (*15*) except that the check-valve assembly was removed.

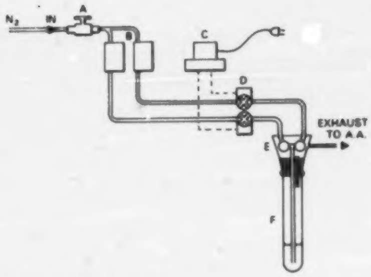

Figure 1. Diagram of hydride generator

(A) single stage, low pressure gas regulator, (B) pressurized reagent bottles, (C) 4-cam motor driven timer (90 sec), (D) Teflon-bodied, relay actuated solenoid valves, (E) reaction head with Teflon metering valves, (F) reaction cell

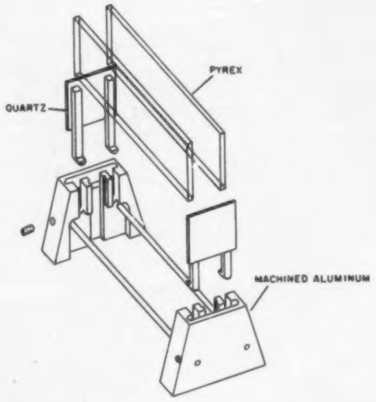

Figure 2. Flame shield for Boling burner head

Reagents. The $NaBH_4$ reducing solution is made by dissolving 4 g of the powder or pellets (Ventron Corp.) in approximately 50 ml of NaOH (10% w/v) solution. This solution is then diluted to 100 ml with 10% (w/v) NaOH. The strong base stabilizes the borohydride solution. For the arsenic and antimony determinations, a 10% (w/v) NaI prereductant solution is used. An acid diluent solution is made by mixing 50 ml of concentrated H_2SO_4 with 300 ml of distilled-deionized water. To this mixture is added 300 ml of concentrated HCl, followed by dilution to 1 l. with distilled-deionized water.

Sample Preparation. The sample of food or biological tissue (1–3 g, dry weight) is weighed into a 100-ml Kjeldahl flask, and 30 ml of a (4:1:1) mixture of concentrated, reagent grade HNO_3, H_2SO_4, and $HClO_4$ is added to the flask. At least one reagent blank consisting of 30 ml of the ternary acid mixture is prepared with each set of 10–12 samples. The sample oxidation is carried out using one or more 6-unit, micro-Kjeldahl digestion racks equipped with a glass manifold, water-cooled condenser, receiving flask, and dilute (10% w/v) NaOH scrubbing tower. The sample–acid mixture is initially heated very gently. After the sample foaming subsides, the temperature is raised to produce steady boiling. Sample charring is avoided by cautious heating during the $HClO_4$ reaction. If slight charring does occur, analyte loss can be prevented by immediate addition of small (1 ml) increments of concentrated HNO_3 and/or rapid cooling of the sample–acid mixture in an ice water

Table I. Operating Parameters

Element	As	Se	Sb	Te
Source	EDL	EDL	EDL	HCL
Source power or current	8 watt	6 watt	7 watt	30 mA
Slit width, mm	3	3	0.3	1
Spectral band width, nm	2.0	2.0	0.2	0.7
Wavelength, nm	197.2[a]	196.0	217.6	214.3

[a] The 193.7-nm resonance line of As is about twice as sensitive as the 197.2-nm line and can be employed with some sacrifice of linear range.

bath. Excess $HClO_4$ is boiled off and the residual H_2SO_4 heated strongly to fumes of sulfur trioxide. G. F. Smith's monograph on the use of perchloric acid may be consulted for a more thorough treatment of necessary precautions (*16*). These vigorous acid-oxidation conditions are required both to prevent volatilization loss of the analyte(s) and to oxidize the sample completely. Unoxidized organic moieties in the digest appear to alter the rate of release of the hydrides during the determinative step of the procedure. The digestion is normally complete in 1.5 to 2 hr.

The digests, when cooled to room temperature, are transferred to 100-ml volumetric flasks. Concentrated HCl, 30 ml, is added to each flask and the solution diluted to 100 ml with distilled-deionized water.

Instrumental Conditions. With the burner drain tube tightly stoppered, the hydrogen diffusion flame is established, using a hydrogen flow rate of approximately 2 l./min (10 psig) and a nitrogen diluent flow rate of about 6 l./min (30 psig). The nitrogen is introduced through the auxiliary oxidant port of the burner, and the normal nebulizer tube is removed from the chamber and closed off. The hydrides are introduced through the nebulizer port. Optimization of the absorption signal is normally obtained by adjusting the position of the burner head to a height just below the optical path of the line source. Typical instrument parameters are shown in Table I.

Prior to the actual determinations, the duration and flow rates of the $NaBH_4$ introduction and distilled water wash, and the duration of the rest period were adjusted to ensure complete reaction of the analyte(s) and to maximize the absorption signal. Typical $NaBH_4$ solution and distilled water wash flow rates were 24–32 and 20–40 ml/min, respectively. The latter was not critical since it served only to rinse unspent $NaBH_4$ from the capillary. The flow rates were achieved by regulating the pressure (3–5 psig) on the reagent reservoirs and adjustment of the Teflon needle valves in the reaction head. The 4-cam timer (90 sec/rev) which controlled the two normally closed solenoid valves by actuating microswitches, was adjusted to provide 15 sec open (on) time for the $NaBH_4$ solenoid, 5 sec rest period, and 5–15 sec for the distilled water (wash cycle) solenoid. The resulting 6–8 ml $NaBH_4$ addition resulted in well defined, reproducible absorption peaks for each analyte. Sufficient accuracy was obtained by peak height measurement. Signal integration was possible but was not used for routine analysis. Correction for non-specific background absorption proved entirely unnecessary.

Determination of Arsenic or Antimony. An aliquot of the acidified sample digest (maximum of 20 ml, which is equivalent to 1 g of sample when 5 g (wet weight) is digested) is transferred to an 8-in test tube reaction cell and diluted to 20 ml with the acid diluent as necessary. The NaI prereductant (10% w/v) is added to the reaction cell: 0.5 ml is sufficient to reduce As^{5+} or Sb^{5+} to the trivalent state. A minimum of 1-min reaction time is required to prereduce the As and Sb. The test tube is affixed to the reaction head of the hydride generator, and the timer is actuated. The reaction gases are transported to the burner, and the transient absorbance signals are recorded. Standards, typically ranging from 0.05 to 0.70 μg As or Sb, are prepared by appropriate microliter additions of a 10 μg/ml mixed As–Sb stock solution (prepared daily in 30% v/v HCl) to 20-ml volumes of the acid diluent. Standards and reagent blanks are treated with the NaI prereductant prior to hydride generation.

The prereductant is essential to the generation of stibine, SbH_3, under the uniform conditions of acidity (5% H_2SO_4, 30% HCl) used throughout for As, Sb, Se, and Te. Arsine, AsH_3, is quantitatively produced either in the presence or absence of the NaI, i.e., quantitative reduction of As^{5+} or As^{3+} is achieved by the $NaBH_4$. However, the appearance of the As absorption signal is delayed and the signal duration is somewhat longer without the NaI prereductant (Figure 3). The peak areas, integrated over 30 sec, are identical for As^{5+} compared with As^{3+} initial oxidation states.

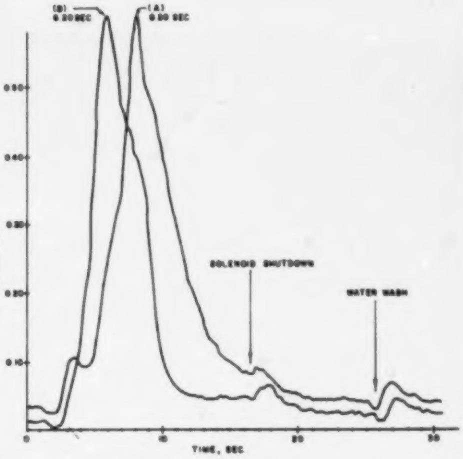

Figure 3. Absorbance vs. time peaks for 0.5 μg As

(A) without NaI prereductant, (B) with NaI prereductant. Peak areas are identical over 30-sec integration. Base lines are offset to avoid overlap

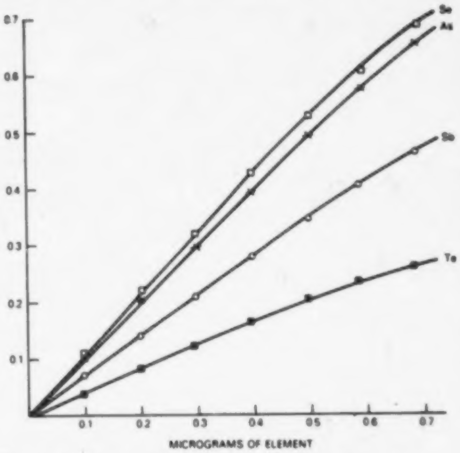

Figure 4. Analytical calibration curves for As, Se, Sb, and Te

Determination of Selenium or Tellurium. Sample, blank, and standard aliquots for Se or Te determination are treated just as those for As or Sb determination with the important exception that no prereductant is added. A prereductant would prevent generation of H_2Se or H_2Te by possible reduction to the elemental form.

RESULTS AND DISCUSSION

Sensitivity and Linearity. Both the sensitivity and the linearity are illustrated in Figure 4. The analytical calibration curves for As, Se, and Sb are all linear to about 0.5 μg of the element when using EDL's as the primary source, peak height measurements, and moderate instrument damping ($\tau = 1$ sec). Under the same conditions, but using an HCL as primary source, the Te calibration curve is linear to about 0.4 μg.

Table II. Analysis of NBS Reference Materials, ppm (dry weight)

	AAS (Hydride)[a]	NBS[b]	Independent NAA
Orchard Leaves (SRM 1571)			
As	11 ± 1	11 ± 2	...
Se	0.055 ± 0.009	0.08 ± 0.01	...
Sb	2.99 ± 0.05	...	3.0[c]
Bovine Liver (SRM 1577)			
As	0.049 ± 0.006	0.055[d]	...
Se	0.98 ± 0.01	1.1 ± 0.1	...
Sb	Not Detected	...	0.034[e]
Tuna[f]			
As	3.3 ± 0.2	4.6 ± 0.3	3.6 ± 0.2[g]
Se	3.6 ± 0.1	3.3 ± 0.3	...

[a] Mean and standard deviation based on the analyses of three replicate 1-g samples. [b] Estimate of uncertainties in no case less than 95% confidence limits. [c] *(19)*. [d] NBS Informational value *(17)*. [e] *(20)*. [f] NBS proposed research material. NBS informational As and Se values from ref *(18)*. [g] FDA NAA value.

Table III. Arsenic Confirmation Analyses, ppm (dry weight)

Sample	Neutron activation[a]	Spectrophotometric[b]	AAS (hydride)[c]
Haddock	40 ± 2	40.1	37 ± 3
Perch	9.0 ± 0.4	8.3	7.5 ± 0.4
Flounder	19.0 ± 0.9	15.8	15.3 ± 0.7
Cod	12 ± 1	11.3	11 ± 2

[a] NAA based on 1-2 analyses. [b] Single analysis. [c] Based on 5 replicate analyses over a 4-month period.

Table IV. Selenium Confirmation Analyses, ppm (dry weight)

Sample	Neutron activation[a]	Fluorometry[b]	AAS (hydride)[c]
Haddock	1.6 ± 0.4	1.6	1.6 ± 0.4
Perch	2.2 ± 0.2	2.3	2.6 ± 0.3
Flounder	0.9 ± 0.3	0.9	1.2 ± 0.2
Cod	1.2 ± 0.2	1.2	1.4 ± 0.4

[a] NAA based on 3–5analyses. [b] Single analysis. [c] Based on 5 replicate analyses over a 4-month period.

Rather than use the definition of sensitivity common to practicing atomic absorption spectroscopists, i.e., the concentration of analyte, in µg/ml, which will produce 1% absorption (0.0044 *A*), the authors prefer the use of the "slope" of the linear portion of the analytical calibration curve. For Se, As, Sb, and Te, the sensitivities are 1.10, 1.00, 0.70, and 0.40*A*/µg, respectively.

Accuracy. The accuracy of the analytical method was established by: (1) successful determination of As, Se, and Sb in NBS Standard Reference Materials *(17)*; (2) agreement of results obtained by hydride generation–atomic absorption spectrometry with totally independent techniques; and (3) quantitative recovery of analytes added to a variety of foods. The third approach was especially important for Sb and Te where native levels of the elements in foods or biological tissues either were not detected or were too low to be quantitated.

Results of the analysis of NBS SRM 1571 (Orchard Leaves) and SRM 1577 (Bovine Liver) for As, Sb, and Se are given in Table II. Results are also given for a Tuna which will be an NBS Research Material. Since the Tuna has not been certified, all of the tentative NBS values must be considered as informational values only *(18)*. With the possible exception of Se in Orchard Leaves, and As in Tuna, the results obtained by the hydride evolution method agree quite well with NBS certified or informational values. FDA independent NAA analysis gave an As value for the Tuna of 3.6 ± 0.2 ppm. The Orchard Leaves, which contain rather large amounts of As and Sb (NAA value) *(19)* and relatively little Se, and the Bovine Liver, which contains a substantial amount of Se but little As and Sb (NAA value) *(20)*, provide excellent examples of the accuracy of the method over a large range of concentrations for two very different natural materials.

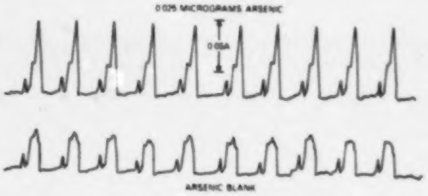

Figure 5. Typical precision of measurement for 10 replicate standard solutions

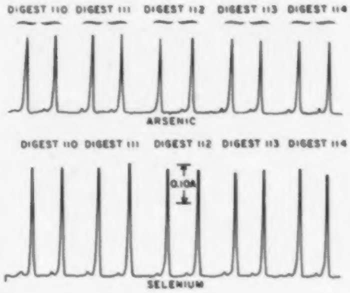

Figure 6. Reproducibility of the determination of As and Se in oyster meats: duplicate measurements

Further confirmation of accuracy is given by the agreement among values obtained by independent analytical methods shown in Tables III and IV. Frozen fillets of fish were purchased, coarsely ground with a meat grinder, blended and lyophilized. The dried products were further ground and blended prior to analysis by γ ray spectrometry (NAA), fluorometry (for Se), absorption spectrophotometry (for As), and atomic absorption spectrometry (hydride volatilization). The results agree well within experimental error. During the course of hundreds of analyses, a large volume of recovery data was collected. The recovery data were obtained by a single addition of the analytes to each commodity. In general, enough analyte was added to fortify the samples by amounts ranging from approximately the native level to as much as fivefold greater than the native level. Since Sb and Te either were not detected or could not be quantitated in any food, additions were made at the 1-µg level. For a wide variety of foods and spiking levels, the relative recoveries were 98 ± 5% for As, 104 ± 7% for Sb, 106 ± 6% for Se, and 100 ± 7% for Te.

Precision and Detection Limits. Ten replicate measurements each of the As peak for a standard solution containing 0.025 µg of the analyte and the reagent blank solution were made (Figure 5). The shoulder on the trailing (left) side of the analyte peak corresponded to the $NaBH_4$ solenoid shut-down whereas the small peak further to the left of each analyte peak resulted from the distilled water wash cycle. The average absorbance of the standard was

Table V. Interlaboratory Study: Arsenic,[a] ppm (dry weight)

Laboratory	Haddock	Perch	Flounder	Cod	Tuna	Eggs	Chicken livers
1	36.0	8.1	16.1	11.1	3.3	<0.1	<0.1
2	35.1	7.2	14.8	10.2	3.2	n.d.[b]	n.d.
3	...	6.6	14.2	10.1	3.4	n.d.	n.d.
4	34.5	6.7	16.3	10.9	3.4	n.d.	0.35
Av (Std dev)	35.2 (0.8)	7.2 (0.7)	15.4 (1.0)	10.6 (0.5)	3.3 (0.1)	...	...

[a] Individual values are single analyses. [b] Not detected.

Table VI. Interlaboratory Study: Selenium,[a] ppm (dry weight)

Laboratory	Haddock	Perch	Flounder	Cod	Tuna	Eggs	Chicken livers
1	1.3	2.3	0.9	1.1	1.6	1.1	2.1
2	1.5	2.8	1.0	1.5	2.7	0.9	2.0
3	1.6	2.4	1.1	0.9	1.9	1.0	1.7
4	1.1	2.2	1.1	1.4	1.9	0.9	1.9
5	1.1	2.2	1.3	0.5	1.6	1.0	2.2
Av (Std dev)	1.3 (0.2)	2.4 (0.2)	1.1 (0.1)	1.1 (0.4)	1.9 (0.4)	1.0 (0.1)	2.0 (0.2)

[a] Individual values are single analyses.

0.0709 with a standard deviation of 0.0011 (1.55% relative standard deviation). For the reagent blank, the respective values were 0.0362 and 0.0020 absorbance units (5.52% relative standard deviation). Similar precision data were obtained for the other elements, Sb, Se, and Te.

The precision does not deteriorate appreciably for the overall determination, as evidenced in Figure 6, which shows the reproducibility of five separate analyses of an oyster meat homogenate for As and Se. Duplicate measurements are shown for each of the five digest solutions. The approximate amounts of As and Se represented in Figure 6 are between 0.2 and 0.3 μg. The relative standard deviations for As and Se, calculated from the average of the duplicate measurements, are 3.0% and 2.1%, respectively.

Detection limits are normally defined on the basis of variations in the background signal. The most common definition is the concentration, or absolute amount, of analyte required to give a signal-to-noise ratio of 2 (i.e., 2 times the standard deviation of the background signal). It is worthwhile to distinguish between the method detection limits and the instrumental (determinative step) detection limits. The former includes the latter and all other sources of variance relating to the preparation of a sample for analysis.

The instrumental detection limits for As, Sb, Se, and Te were 3, 2, 2, and 11 ng, respectively using EDL primary sources. In order to estimate the method detection limits for As, Se, and Sb, four 5-g samples of strained baby foods were digested and treated as described earlier. Five replicate measurements were made for each of the four identical sample solutions. Twenty replicate determinations of the total reagent blank were made to determine its mean absorbance and the standard deviation. The samples were found to contain insignificant amounts, if any, of the analytes, and the standard deviations of the sample and the sample reagent blank were statistically equivalent for each element. The major contributor to the As reagent blank was the $NaBH_4$/NaOH solution while the Se reagent blank was due to the H_2SO_4 primarily. Sources of the Sb and Te reagent blanks were not investigated.

In keeping with error propagation theory, the standard deviation for the difference between sample and sample reagent blank is greater than the individual equivalent standard deviation by a factor of $\sqrt{2}$. Therefore, the method detection limits are 7 ng for As, 6 ng for Sb, and 16 ng for Se. Since each 20-ml aliquot represents 1 g of sample, the method detection limits based on the sample weight are 7, 6, and 16 ppb and on solution volume are 0.35, 0.30, and 0.80 ng/ml, respectively.

A fixed set of conditions were employed for the detection limit measurements. While some of these parameters were optimized for maximum analyte absorption signals (fuel and N_2 flow rates, burner height, EDL power levels, etc.) others were not (acid concentration, $NaBH_4$/NaOH concentration and flow rates, etc.). Since the hydrides decompose easily in the flame, the burner position and fuel and diluent gas flow rates for maximum absorption were the same for all analytes. Therefore, the detection limits reported here should not be regarded as the best obtainable using the hydride generator.

Method Reliability. The reliability of the method was tested by five participating laboratories, including the authors', using the same semiautomatic hydride generator. Seven homogenized, lyophilized samples (five different fish species, chicken liver, and eggs) were distributed to each laboratory. Results for As and Se are given in Tables V and VI. The participating laboratories were not asked to determine either Sb or Te in the seven samples. The results are based on a single analysis by each laboratory. While not excellent, the majority of results agree within 10–20% of each other. No explanation was sought from the participants for the apparent outliers.

Interference Study. Since volatilization of the analyte separates it from the majority of matrix constituents except other volatile species, spectral interferences were neither expected nor found. Interferences, however, might arise if the rate of reaction producing the hydrides were altered, for example, by constituents of the digested sample. None of the five cationic species tested, Cu^{2+}, Fe^{3+}, Sn^{2+}, VO^{2+}, and Zn^{2+}, produced significant change in analyte absorption at cation concentration up to 1000 μg/g (based on sample weight). Similarly, residuals of HNO_3 or $HClO_4$ from the sample oxidation did not interfere. Interferences between hydride-forming elements were not examined directly. However, we concluded that native amounts of As and Se, which vary substantially in foods, would not interfere with each other on the basis of the data presented in Tables II, III, and IV. The major interference was apparently incompletely oxidized organic moieties in the sample solution. Thorough sample digestion using the ternary acid mixture rather than HNO_3 and $HClO_4$ alone eliminated this interference.

Potential Extension to Other Elements. Other investigators have shown that Bi, Ge, and Sn can be volatilized from acid solution using $NaBH_4$ to generate their hydrides (*10–12, 21*). The authors of this article have not studied the behavior of these elements in the depth necessary to prove that they can all be determined in foods. However, if these elements are not lost during sample oxidation, it is likely that quantitative measurements may be obtained. Analytical calibration curves were obtained using the semiautomatic hydride generator for Bi, Hg, and Sn. BiH_3 was quantitatively volatilized from a solution of 30% (v/v) HCl and 5% (v/v) H_2SO_4. The sensitivity was 0.71 *A*/μg Bi for the 223.1-nm resonance line using an EDL primary source (8-watt, 0.7-nm band pass). Hg was quantitatively generated as the metal from a solution of 30% (v/v) HCl and 5% (v/v) H_2SO_4. The sensitivity, using a 10-cm cell in place of the hydrogen diffusion flame, was 0.55 *A*/μg at the 253.7 nm line. An HCL operated at 6 mA was the primary source (0.7-nm band pass). It should be noted that Hg was generated as the atomic vapor from acid solutions other than HCl–H_2SO_4 mixtures, e.g., HNO_3, H_2SO_4, or $HClO_4$. Sn was generated as SnH_4 from 5% (v/v) $HClO_4$ using $NaBH_4$ in 1% (w/v) NaOH. The sensitivity was approximately 1.75 *A*/μg using an EDL operated at 8 watts (224.6 nm, 0.7-nm band pass). Of the seven elements investigated, only Sn was affected appreciably by variations in acid concentration. This observation has been reported previously (*11, 21*).

CONCLUSION

We have shown that the determination of As, Sb, Se, and Te in foods utilizing a semiautomatic hydride generator is accurate, precise, and sensitive. As with fully automated analytical instruments, the semiautomatic hydride generator affords relative freedom from analyst carelessness, relatively high speed of analysis, and excellent precision. The detection capabilities are comparable to those obtainable via instruments based on peristaltic pumping systems which are considerably more complex and costly than the semiautomatic hydride generator described in this paper.

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Matrix Effects in the Determination of Copper and Manganese in Biological Materials Using Carbon Furnace Atomic Absorption Spectrometry

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A systematic investigation of the interference of 1 to 1000 ppm of the chlorides, nitrates, phosphates, and sulfates of H, Na, K, Ca, Mg, Zn, and La (except $CaSO_4$) on Cu and Mn is performed. A study of the peak form of the recorded absorption signals is carried out and a comparison is made between peak area and peak height. Sharper and narrower peaks are observed for interferences resulting in an increase of the absorption signal. This points to a faster atomization of the analyte in these cases. Because the peak form was unaffected in the case of negative interferences, the effect of the times and temperatures for drying, ashing, and atomization was investigated. This shows that these interferences are at least partially due to occlusion of the analyte in the matrix.

In the past few years, matrix effects encountered with nonflame atomization devices have been investigated by several authors (for instance *1–8*). Nevertheless, much work remains to be done to elucidate the origin and nature of the different observed interactions. A comparison of the data given by the various authors is difficult because of the diverse atomization designs used, since atomization tem-

Rapid Digestion and Flameless Atomic Absorption Spectroscopy of Mercury in Fish: Collaborative Study

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A collaborative study of the determination of mercury in fish has been completed in which wet oxidation of fish tissue in nitric acid, using vanadium as a catalyst, is compared with the AOAC official final action digestion technique, 25.103–25.105, involving a nitric-perchloric acid mixture. The study used tuna fish samples of known mercury content and included spike recovery studies in which methyl mercury solutions of known composition were provided to each laboratory. The study was designed to provide recovery information that bracketed the regulatory level of mercury in fish. The results indicate that the proposed digestion method is at least as precise and accurate as the AOAC method. The proposed method is also more rapid and less hazardous. It has been adopted as official first action.

The current official final action method for determining mercury in fish (1) requires a lengthy digestion step that may be hazardous due to the use of perchloric acid. More rapid wet oxidation methods that do not completely destroy organic matter have been proposed (2–4). Among these is that described by Malaiyandi and Barrette (4), which relies on the catalytic effect of vanadium to speed oxidation of organic matter in nitric and sulfuric acids. This procedure has been modified for use in the reflux digestion apparatus described in the AOAC method (1). A previous collaborative study of the vanadium-catalyzed method was conducted by the present authors (unpublished data, 1972). This study demonstrated the general efficacy of the proposed method; however, the design of the study was defective from 2 standpoints. Because each participating laboratory provided its own fish tissue samples, the results could not be statistically compared, and the study did not adequately bracket the regulatory concentration of 0.5 ppm. Since accuracy estimates were based only on spike-recovery data, reliable estimates of the intralaboratory error could not be obtained. Therefore, the study was repeated, using an improved design.

Collaborative Study

Uniform samples of lyophilized tuna prepared by the National Bureau of Standards (NBS) and sealed in cans were provided to each of the 11 collaborators. NBS, on the basis of analysis by several analytical techniques, reported the mercury content as 1.0 ppm on a dry weight basis (5). This is equivalent to 0.30 ppm on a wet weight basis. Each collaborator was also provided with 4 sealed ampoules containing solutions of known mercury concentrations as methyl mercury chloride to be used for spike-recovery studies. Laboratories were instructed to reconstitute the tuna by adding 3.5 ml distilled water to 1.5 g (dry weight) portions, equivalent to 5.00 g fresh fish (70% water). One ml of each spiking solution was to be added to each of 4 reconstituted samples while the fifth sample was to be analyzed as received. The mercury concentration levels at which the 4 samples were spiked were: 0.00 (blind), 0.20, 0.40, and 0.70 ppm (wet weight basis). The analyses of 2 sets of these 5 portions were to be performed on the same day by both the AOAC and the proposed digestion methods. The entire analytical procedure (by both methods) was to be repeated on another day.

Mercury in Fish

Flameless Atomic Absorption Method
Official First Action

(Rinse all glassware before use with HNO_3 (1+9). *Caution: See* **51.019**, **51.026**, **51.030**, and **51.079**.)

25.C01 ***Apparatus***

See **25.103(a)**, **(b)**, **(e)**, and in addn:

(a) *Boiling stones.*—6–8 mesh (SGA Scientific Inc., No. D-7325).

(b) *Gas inlet adapter.*—₮ 24/40 (Kontes Glass Co., No. K-181000). Cut off end of glass tube which extends downward from adapter and affix gas dispersion tube with fritted cylinder (Corning Glass Works, No. 39533, porosity 12C).

(c) *Trap.*—Construct from broken bulb of 15 ml

This is the 1976 report of the Associate Referee, R. K. Munns.

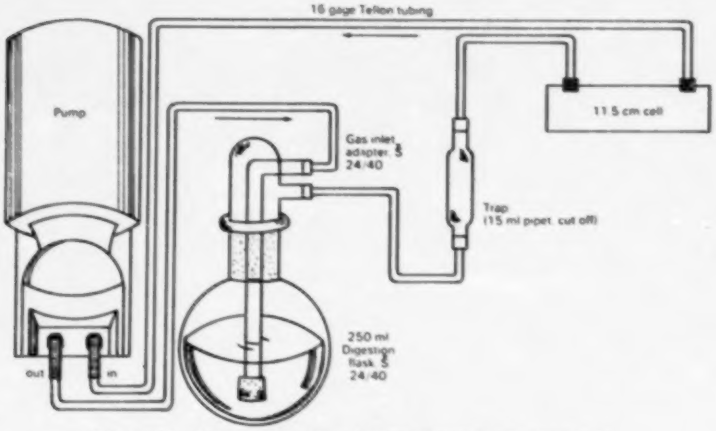
16 gage Teflon tubing
Pump
out
in
Gas inlet adapter $ 24/40
11.5 cm cell
Trap (15 ml pipet, cut off)
250 ml Digestion flask $ 24/40

FIG. 25:C1—Apparatus for flameless atomic absorption analysis

pipet and place between digestion flask and cell, replacing flask of Fig. 25:02, to trap overflow (*see* Fig. 25:C1).

(d) *Water condenser.*—12–18 (id) × 300 mm Liebeg condenser with Ŧ 24/40 joint. Modify by making indentations in glass between lower std taper and H_2O jacket with pointed C rod. Indent glass to hold 6 mm Raschig rings. Add 8–10 rings to condenser and cover with ⅛" (3.17 mm) id glass helices (SGA Scientific Inc., No. JD-5360) to ht of 90 mm.

25.C02 ***Determination***

Weigh 5.0 g (wet wt) thoroly mixed fish sample into digestion flask, **25.103(e)**. Rinse neck of flask with <5 ml H_2O, if necessary. Add ca 20 boiling stones, **(a)**, 10–20 mg V_2O_5, and 20 ml H_2SO_4-HNO_3 (1+1). Quickly connect flask to condenser, **(d)**, and swirl to mix. Circulate cold H_2O thru condenser during digestion. Apply sufficient heat (luminous flame is suitable) to produce low initial boil (ca 6 min) and finish digestion with strong boil (ca 10 min). Swirl flask intermittently during digestion. No solid material should be apparent except for globules of fat after ca 4 min.

Remove flask from heat and wash condenser with 15 ml H_2O. Add 2 drops 30% H_2O_2 thru condenser and wash into flask with 15 ml H_2O. Cool digested fish soln to room temp. by placing flask, still connected to condenser, in beaker of H_2O. Disconnect flask, rinse ground joint with H_2O, and quant. transfer digest to 100 ml vol. flask. Ignore solidified fat; it does not interfere. Carefully rinse digestion flask with several portions H_2O and dil. to vol. with rinse H_2O.

Pipet 25 ml soln into original digestion flask and add ca 75 ml dilg soln, **25.104(b)**. Proceed as in **25.105**, beginning "Adjust output of pump . . .", except aerate ca 1 min and use 0, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 μg/ml Hg std solns. 1 μg/ml std should give $A \geq 0.400$.

Results and Recommendation

The results for the total mercury concentrations reported by each laboratory are given in Tables 1 and 2. These data demonstrate that the proposed and the official methods produce consistently comparable results. The descriptive statistics for the analysis of the data, by method and spike level, are summarized in Table 3. The data analyses given were based on the statistical techniques described by Youden (6). The average per cent recoveries given in Tables 1 and 2 were determined by subtracting the mean residue concentration from the mean residue + spike concentration. These statistics were used to compare the 2 methods at each analytical concentration level (6). The conclusions derived from these tests are as follows:

(*1*) There was no significant difference between the method averages at any spike level ($P > 0.05$ in all cases). This verifies that statistically equivalent analytical results are obtained with either method.

(*2*) There was significant variation among the laboratory averages at each spike level ($P < 0.01$ for the 0.00, 0.40, and 0.70 ppm spike levels and $P < 0.05$ for the 0.20 ppm spike level). As might

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This method was approved as an interim official method by the General Referee on Metals and Other Elements and by Subcommittee E. The Association adopted the method at the 1976 Annual Meeting. *See* (1977) *JAOAC* **60**, 407.

Table 1. Collaborative results (μg/g, wet weight) for the determination of mercury by the proposed method

Coll.	Anal. day	Residue	Residue + blank spike	Residue + 0.2 ppm spike	Residue + 0.4 ppm spike	Residue + 0.7 ppm spike
1	1	0.28	0.28	0.45	0.62	0.94
	2	0.30	0.30	0.48	0.60	0.94
2[a]	1	0.14	0.17	0.38	0.34	0.53
	2	0.27	0.30	0.37	0.48	0.54
3	1	0.23	0.25	0.42	0.60	0.87
	2	0.25	0.25	0.43	0.61	0.88
4	1	0.28	0.28	0.47	0.64	0.86
	2	0.26	0.26	0.43	0.62	0.87
5	1	0.23	0.23	0.40	0.56	0.83
	2	0.21	0.20	0.35	0.50	0.78
6	1	0.26	0.26	0.45	0.63	0.92
	2	0.27	0.24	0.43	0.61	0.91
7	1	0.23	0.26	0.44	0.64	0.90
	2	0.26	0.27	0.44	0.60	0.93
8	1	0.26	0.30	0.50	0.67	0.92
	2	0.27	0.29	0.47	0.66	0.89
9	1	0.39	0.40	0.65	0.89	1.26
	2	0.38	0.38	0.64	0.85	1.25
10	1	0.29	0.31	0.42	0.68	0.95
	2	0.25	0.28	0.45	0.54	0.87
11	1	0.26	0.35	0.57	0.67	1.22
	2	0.34	0.37	0.51	0.69	0.88
Mean[b]		0.2750	0.2880	0.4700	0.6440	0.9435
Std dev.[b]		0.0471	0.0521	0.0747	0.0906	0.1355
Av. rec., %		—	—	97.5	92.3	95.5

[a] Data were eliminated from statistical analysis as outliers.

[b] Underlined numbers indicate general lack of significance but they were carried for statistical analysis purposes.

be anticipated, the variation in interlaboratory results was greater than that in the intralaboratory results.

(*3*) The precision of the 2 methods as measured by the within-laboratory repeatability was equal ($P > 0.05$) for the residue, residue + blank spike, and residue + 0.70 ppm spike samples. However, the precision of the AOAC method was significantly less ($P < 0.05$) than that of the proposed method for the residue + 0.20 ppm and the residue + 0.40 ppm spiked samples. Moreover, when the precision estimates were pooled (6) for all levels, the precision of the AOAC method was significantly less than that of the proposed method ($P < 0.05$). Therefore, it may be generally concluded that more precise (within-laboratory) analyses may be associated with the proposed method. (Compare values of CV 2 for 2 methods given in Table 3.)

(*4*) The interaction between laboratory and method was insignificant for all spike levels ($P > 0.05$).

Based on these tests, it may be generally concluded that the proposed method is at least as good as the AOAC method. Since NBS had reported the mercury content, the average accuracy of the collaborative results could be estimated as shown in Table 4. These results indicate that the mean accuracies of the methods are equivalent within experimental error as indicated by the standard deviation estimates given (Table 3). This conclusion, combined with mean per cent recovery data for the spike levels (Table 3), further indicates that both methods are accurate within experimental error.

In view of the fact that the proposed digestion-analysis method is subject to less hazard, more convenient to use, and at least as good as the present official method, it is recommended that it be adopted as official first action.

Acknowledgments

Appreciation is expressed to the Office of Standard Reference Materials, NBS, Washing-

Table 2. Collaborative results (μg/g, wet weight) for the determination of mercury by the AOAC method

Coll.	Anal. day	Residue	Residue + blank spike	Residue + 0.2 ppm spike	Residue + 0.4 ppm spike	Residue + 0.7 ppm spike
1	1	0.27	0.30	0.42	0.59	0.89
	2	0.30	0.31	0.46	0.61	0.89
2[a]	1	lost	0.18	0.29	0.53	0.67
	2	0.38	0.34	0.38	0.47	0.54
3	1	0.27	0.25	0.47	0.65	0.90
	2	0.28	0.28	0.47	0.65	0.88
4	1	0.26	0.25	0.44	0.59	0.81
	2	0.20	0.19	0.27	0.45	0.72
5	1	0.27	0.27	0.46	0.63	0.94
	2	0.24	0.24	0.46	0.62	0.87
6	1	0.28	0.26	0.48	0.67	0.76
	2	0.27	0.29	0.45	0.62	0.92
7	1	0.27	0.29	0.49	0.63	0.88
	2	0.24	0.26	0.42	0.58	0.87
8	1	0.27	0.30	0.41	0.69	0.86
	2	0.26	0.30	0.50	0.57	0.87
9	1	0.40	0.39	0.65	0.89	1.24
	2	0.32	0.37	0.54	0.76	1.24
10	1	0.24	0.29	0.49	0.56	0.85
	2	0.21	0.26	0.41	0.45	0.86
11	1	0.28	0.34	0.49	0.60	0.88
	2	0.38	0.37	0.61	0.86	0.68
Mean[b]		0.2755	0.2910	0.4695	0.6335	0.8905
Std dev.[b]		0.0478	0.0486	0.0771	0.1085	0.1527
Av. rec., %		—	—	97.0	89.5	87.9

[a,b] See Table 1.

Table 3. Summary of descriptive statistics for the collaborative study[a,b]

Sample description	Anal. method	$\overline{X}$	Mean rec., %	s	CV 1	CV 2	CV 3
Residue	AOAC	0.2755	—	0.0478	17.35	12.55	15.19
	Prop.	0.2750	—	0.0471	17.12	8.45	16.42
Residue + blank spike	AOAC	0.2910	—	0.0486	16.73	7.50	16.23
	Prop.	0.2880	—	0.0521	18.08	4.91	18.21
Residue + 0.2 ppm spike	AOAC	0.4695	97.0	0.0771	16.42	13.24	13.68
	Prop.	0.4700	97.5	0.0747	15.89	4.99	15.90
Residue + 0.4 ppm spike	AOAC	0.6335	89.5	0.1085	17.13	13.02	14.68
	Prop.	0.6440	92.3	0.0906	14.07	5.83	13.79
Residue + 0.7 ppm spike	AOAC	0.8905	87.9	0.1527	17.48	7.21	14.74
	Prop.	0.9435	95.5	0.1355	14.36	8.44	13.34

[a] $\overline{X}$ = average concentration (units) reported; s = standard deviation of the method; CV 1 = coefficient of variation (relative standard deviation) for the reproducibility of the method, %; CV 2 = coefficient of variation for the within-laboratory repeatability, %; CV 3 = coefficient of variation for a laboratory average, %.

[b] Underlined numbers indicate a general lack of significance but they were carried for statistical analysis purposes.

ton, DC, for providing the fish tissue samples used in this study; to Rodney K. Skogerboe, Science Advisor, Food and Drug Administration, Denver, CO for technical guidance and planning; to John Fiorino and Foster D. McClure, Food and Drug Administration, Washington, DC for statistical assistance; and to the following collaborators who participated in this study: J. M. Owens, Lauelles Testing Laboratories, Seattle, WA; and, from the Food and Drug Adminis-

Table 4. Summary comparison of the mean per cent recoveries (accuracy)[a] of the methods

Sample description	AOAC	Prop.
Residue	91.8	91.7
Residue plus blank spike	97.0	96.0

[a] Mean per cent accuracy was estimated from 100 (mean concentration)/provisionally indicated concentration (5).

tration—K. W. Barnard and K. Couture, Boston, MA; R. L. Carr, Cincinnati, OH; E. H. Corrigan and M. Reino, Buffalo, NY; J. E. Davenport and M. Jakes, Atlanta, GA; M. Falcone and T. C. Konecy, Philadelphia, PA; F. E. Hons and M. Jeffus, Dallas, TX; J. La Rose, Seattle, WA; D. E. Melchior, Minneapolis, MN; H. J. Miller and R. Marts, Baltimore, MD; J. L. Moor, San Francisco, CA; M. E. Orlando, Los Angeles, CA; J. E. Roybal, Denver, CO; B. J. Salmon, Detroit, MI; J. F. Weeks, Jr, New Orleans, LA. Names include some people who participated in an earlier study on the same subject.

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4.5.2 Quality Control Procedures

Quality control activities required for the analysis of trace elements in biological materials are described below in some detail. In addition, the standardization and calibration procedures described in the standard analytical methods are to be followed in these analyses. A summary of the type, frequency, control limits, and corrective action for these QC activities is given in Table 4-4.

A. Laboratory Control Standards

For all methods, laboratory control standards (LCS) will be employed to monitor systematic method and operator errors. The LCS, generally, is a solution of one or more analytes of known concentration in reagent water which is carried through the entire sample preparation and analysis procedure.

For these analyses, two types of LCS will be used. The first is the orchard leaves standard reference material (SRM 1571) available from the National Bureau of Standards, Washington, D.C. The certified content of this SRM is given below. The second type of LCS is water spiked with known amounts of the elements of interest. Spiked concentrations should be approximately 4-5 times the analytical detection limit or in the range of the orchard leaves SRM.

SRM 1571 CONTENT

Analyte	Concentration (μg/g)
Arsenic	10
Antimony	2.9
Barium*	(44)
Beryllium	0.027
Cadmium	0.11
Chromium	2.6
Lead	45
Mercury	0.155
Nickel	1.3
Selenium	0.08
Zinc	25

One of each type LCS must be processed for approximately every twenty vegetation samples analyzed. At a minimum, two spikes and two SRM 1571 samples must be analyzed for the full complement of vegetation samples. A control chart must be maintained for each of the analytes.

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*Barium is not certified; value for information only.

TABLE 4-4. INTERNAL QC REQUIREMENTS--TRACE ELEMENTS IN VEGETATION

Operation check	Frequency	Control limits	Corrective action planned
Method blank (reagent water)	One for every 20 samples	No significant concentrations found	Correct for blank Check analytical procedure
Laboratory control standard (LCS)	One of each type for every 20 samples	±2 Standard deviations	Check analytical procedure Analyze second reference sample Invalidate results
Replicate analysis	One of every 10 samples	To be determined	Check analytical procedure Analyze reference sample Invalidate results

Control limits for each of the analytes have been established at ±2 standard deviations. Any measured value that falls beyond the control limits shall trigger an investigation to determine the cause of the deviation and a correction of the problem. Values of environmental measurements from samples processed during that same work shift must be remeasured or not reported unless a satisfactory justification is prepared.

B. Method Blanks

Method blanks (reagent water) must be processed at a rate of approximately one for every twenty samples. This must at a minimum result in two method blanks for the total number of vegetation samples. The method blank must be processed through the entire analytical procedure with the field samples. If common laboratory comtaminants are found in the method blanks and it is determined that the same contaminants are present in the field samples, reported values for these analytes must be reduced by the amount found in the blank.

C. Replicate Analyses

If sufficient amounts of sample are available, intralaboratory precision of the environmental measurements will be evaluated by measurement of one duplicate of every ten samples. A duplicate is a second aliquot of a sample that is carried through the entire laboratory analytical method. These data must be reported with the laboratory results and will be used by EPA in assessing the overall precision of the data.

4.6 INTERFERON IN MOUSE CELLS

4.6.1 Analytical Procedure

Mouse cells are induced to produce interferon by the induction procedure given below and then the interferon produced is assayed by a modification of the technique described in "Computer-Assisted Micro-dye Uptake Human Interferon Assay" by Duvall et al. This paper is included in this section.

The mice are shipped live with food in the cage.

A. Induction Procedure - Type 1 Interferon

1. Mouse spleens removed by sterile technique.
2. Spleen teased apart and cells washed.
3. Erythrocytes lysed by NH_4Cl.
4. Leukocytes washed in PBS-EDTA.
5. Cells counted and resuspended to 10^6 cells in MEM with 5 percent FBS.
6. 0.2 ml of cell suspension added per well of a 96 well sterile microtiter plate. One row of 12 wells inoculated/mouse.
7. Cells primed with marginal and optimal amounts of sendai virus and incubated 2 hours at 37°C.
8. Cells then induced with marginal and optimal doses of sendai.
9. Four wells of each row of cells receive media only to check for spontaneous production.
10. Plates incubated 20 hours overnight.
11. Cells supernatants harvested and assayed for amount of interferon produced.

B. Interferon Assay Procedure

1. Murine & L929 fibroblasts are grown to confluency in 96 well microtiter plates and fed the day before and the day of use with 150 µl of MEM 5 percent FBS. Before use cells are inspected for contamination and confluent growth microscopically.

2. Samples and standards (WHO International Reference Prep. mouse interferon 12,000 IU/ml prepared by National Institute of Allergy and Infectious Diseases, NIH, Bethesda, Maryland, USA, catalog (#G-002-94-511) are stored at -70°C until used.

3. Samples and standards are added to duplicate wells of plates, 1 standard and 4 unknown samples/plate. These are diluted 2 fold vertically down the plate.

4. Cell (+) and viral (-) controls are included on each plate--one row of 8 cells/plate for each control.

5. Cells with sample dilutions are incubated 20-24 hours at 37°C, 5 percent CO_2.

6. All media, sample, and standard dilutions are removed and VSV added to each well except the cell control which receives fresh media. Plates are incubated approximately 24 hours until 90 percent CPE of the viral control is produced in the viral control wells as determined by microscopic examination.

7. 150 µl of neutral red dye in media 5.5×10^{-5} gm/ml is added to all wells and the plates are incubated 1.5-2 hours.

8. Plates are then washed twice with saline and dye extracted from viable cells by the addition of 150 µl of acid ethanol to each well.

9. The developed plate is read spectrophotomitrically on a Titertek Multiskan plate reader and readings fed into the computer for data processing. The titers of each sample are reported on a terminal and recorded, expressed in reference interferon units/ml.

A COMPUTER ASSISTED MICRO-DYE UPTAKE HUMAN INTERFERON ASSAY

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INTRODUCTION

We developed a new computer assisted micro-interferon assay for use in our clinical and research studies, having found the plaque-reduction method too time consuming and cumbersome for our purposes. Several features were desired for a new assay. (A) it sould be simple, easy to use, and suitable for automation, (B) it should yield 50 or more assays/week /technician, (C) it should have sensitivity down to 1 or less reference unit/ml., (D) the assay system should need a sample volume of less than 1 ml for assaying samples at low concentrations of interferon, and (E) it should be reproducible.

Several assays were considered including hemagglutinin yield reduction (1), micro plaque reduction, (2) and micro-tritiated uridine uptake (3) before a modification of the dye-uptake cytopathic effect method was selected (4,5,6).

MATERIALS AND METHODS.

The assay was performed as follows: Human U-Amion cells were grown to confluency in 96 well Micro Test II plates (Falcon Laboratories). One confluent 75 m^2 flask of cells seeded 3 plates, which grew to confluency in approximately 5 days. All additions of media and reagents to plates were done with a 50-200 ul Titertek multi-channel pipette (Flow Labs - Rockville, Maryland). Minimum essential media (Eagles) supplemented with Earles Salts (Grand Island Biological-Grand Island, New York), 5% FBS and 50 ug/ml gentamycin was used in all phases of the assay procedure. The plates were housed in a vented plexiglass box (30.5 x 38.0 x 15.25 cm) with a water reservoir under a well vented raised platform in the bottom. This device maintained a humidity level high enough to prevent peripheral evaporation and uneven distribution of CO_2 over the plates.

The top row of 12 wells in a plate served as the monolayer, negative control, and represented absence of viral cytopathic effect (CPE). The row below it was used as the viral, positive control, and represented 100% CPE. The remaining 6 rows used to assay a reference interferon standard, usually NIH #6-023-901.517, and 5 unknown samples. The medium in the wells was replaced when the cells reached confluency. The standard and unknown samples were simultaneously diluted in triplicate wells across the plate at 4 serial dilutions, usually 2-fold for each sample, using the Titertek. The plates with the sample dilutions were incubated for 20-24 hours. Then, the control media and sample dilutions were aspirated off and a pre-determined dilution of challenge Vesicular Stomatitis Virus (VSV), which will cause 90-95% destruction of the viral control in approximately 24 hours, was added to all wells except the monolayer control. The plates, with challenge virus, were incubated 22 to 26 hours when 90-95% viral cytopathic effect had occurred in the viral control wells. The medium was aspirated off and to each well 150 ul of a neutral red dye solution in media, was added. Neutral red stock solution was prepared by the method of Finter (4). This procedure does not yield a fully solubilized stock solution, therefore, the concentration given above was an estimate. This concentration was chosen because it yielded an optical density of 1.0 in a Sorensen's citrate-ethanol buffer extraction from the monolayer control wells. The plates with dye were incubated an additional 2 hours and then the cells were gently washed twice with phosphate buffered saline (PBS) and the dye was extracted from the viable cells with a solution of equal parts Sorensen's Citrate Buffer, pH 4.2 and 95% ethanol. The volume used of the above extraction fluid was 150 ul per well, when 21 ug/ml concentration of neutral red was used, and 240 ul per well when 33.6 ug/ml was used. The latter concentration was adopted when an automated spectrophometric reading system was incorporated into the assay. The optical density of the extraction fluid from the wells was found to be directly proportional to the concentrations of neutral red used to stain the cells, from 4 ug to 34 ug/ml. Extraction was complete in 30 to 40 minutes.

SECTION IV: IN VITRO TESTING

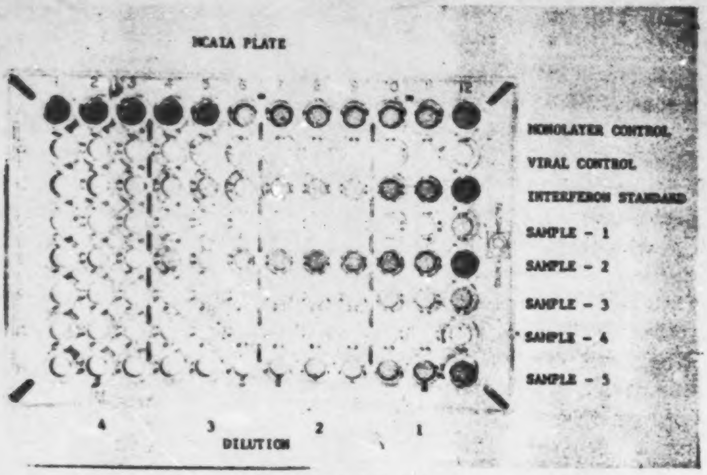

Fig. 1: A micro-dye uptake assay plate.

The increase in CPE for each triplicate of wells, from right to left, occurred as the interferon samples were serially diluted out. The developed plates were stable when sealed with pressure sensitive film (Falcon) and could be stored for several weeks at 4°C before they were read spectrophotometrically.

Viral CPE for each dilution of interferon was quantitated by pooling the monolayer control wells, the viral control wells and each triplicate of wells of the dilutions for each sample, and then they were read spectrophotometrically at 540 nm. The pooled viral control was used as the blank for the plate. To expedite the reading and recording of the samples we recently began using a Gilford Model 250 spectrophometer equipped with a sample programmer, a rapid sampler, and a thermal printer. This method allowed the reading of hundreds of samples a day. (7)

The micro-dye uptake assay generated more data than could be processed manually. It could assay over 75 unknown and 15 reference standard samples, in triplicate, at four dilutions each per week per technician. To overcome the obstacle in data processing a computer program was developed to process the data. The program was written in Fortran IV for use on digital scientific computers. For these experiments a Xerox Sigma 7 computer coupled with a Texas Instruments Silent 700 terminal was used.

The program was designed to process the data from each microtiter plate as a "group" consisting of a (-) monolayer control spectrophotometric reading, and 6 interferon assays or "sets". The set data or individual assay data of a sample correspond to the dilutions and their related readings obtained spectrophotometrically. A group was identified by a number, 1 to 65,535, assay date, VSV lot number, VSV dilution, monolayer control reading, cell generation, standard type and known standard titer. Normally a group contained 1 to 6 sets of assay data. The sets were usually identified with sample information such as source, date of collection, time of collection, and correlation factors (medication, special treatment, etc.). Set 1 of each group was always processed as the reference interferon standard for the group. It was correlated with the known value entered for the standard to generate a reference correlation factor, which converted the titers derived for the rest of the unknown sets (2-6) of a group to reference units.

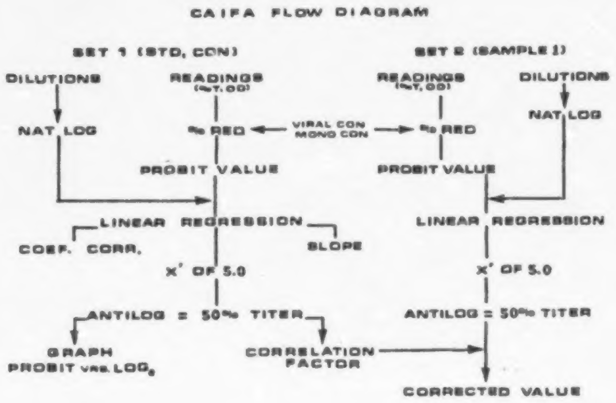
CAIFA FLOW DIAGRAM
SET 1 (STD, CON)
SET 2 (SAMPLE 1)
DILUTIONS
READINGS (%T, OD)
READINGS (%T, OD)
DILUTIONS
NAT LOG
% RED
VIRAL CON
MONO CON
% RED
NAT LOG
PROBIT VALUE
PROBIT VALUE
LINEAR REGRESSION
LINEAR REGRESSION
COEF. CORR.
SLOPE
X' OF 5.0
X' OF 5.0
ANTILOG = 50% TITER
ANTILOG = 50% TITER
GRAPH
PROBIT vs. LOG$_e$
CORRELATION FACTOR
CORRECTED VALUE

Fig. 2 - A generalized flow diagram of the mathematical steps performed by the computer of a set-1 reference standard data and set-2 unknown data of a group.

The computer processing of the data from the first 2 sets of a group is summarized in figure 2. The monolayer control reading, the reciprocal of the sample dilutions and the corresponding optical density reading was entered through the terminal. The mono reading represented absence, (100% reduction), of CPE for all calculations on the plate.

The dilutions were converted to their natural logarithms and the % reduction of CPE was calculated for the sample readings from the monolayer control. This % reduction value was then converted to its corresponding probit value (8). The curve generated by the micro-dye assay is sigmoidal as with the plaque reduction method, and by using a modification of the probit analysis method of Jordan the range of linearity was increased (9). The natural log of the dilution and the corresponding probit value of the % reduction of CPE, Y, were brought together and a linear regression was performed. The coefficient of correlation and slope of the regression curve were calculated. From the regression curve X', the natural log of the reciprocal of the dilution, was determined for Y=5.0, which represented 50% reduction of CPE. The anti-log of this value was calculated and represented the non-correlated titer of interferon in the sample. From the titer, a reference correlation factor was derived, (standard known titer/non-correlated titer obtained). It converted subsequent non-reference titers of sets in the group to reference units. The following sets in the group were processed in an identical fashion except they utilized the correlation factor generated by set one.

The computer was programmed with a flexible probit exclusion range, which routinely edited probit values from computation of the linear regression curves which corresponded to less than 13% reduction of CPE and greater than 95% reduction of CPE. These points were plotted but were not used in the determination of the titer of the sample. These values were excluded because the variability in these regions of the curve was high.

After the data was entered and analyzed the program printed out the raw figures, identifications, calculated values, results, and plotted linear regression curves of the sets in a group. A hard copy print out of the computer results for an assay of NIH reference interferon is shown in Figure 3.

The validity of an assay in this system was easily checked by referring to the coefficient of correlation and the slopes of the assays on a plate. Normally, the curves of the assays from the same plate were quite linear and had similar slopes. This is illustrated in Fig. 4. It was possible to detect some errors by examining the assay curves for non-linearity, and for slopes different from that of the standard and the other samples on a plate.

```
GROUP#113 SET#1 PAT#-1 S:  B:00/00/00 COL:00/00/00 AT 0

COR GPRS:

L.R. FIGURES  CC=-.999 SLOPE=-1.159 X'OF Y=9.829 eX'=18572.659

RANGE 3.9197 THROUGH 6.5548

-- -DILU- --RATIO--- --READING-- -%REDUCTION- --PROBIT--
 1    1   1:3000.00           40       98.3607      7.1345
 2    2   1:6000.00           45       90.1639      6.2930
 3    3   1:12000.00          57       70.4918      5.5388
 4    4   1:24000.00          77       37.7049      4.6866

TITER*FACTOR=  20000.00 TITER=  18572.66 FACTOR=      1.08
GRAPH?Y
```

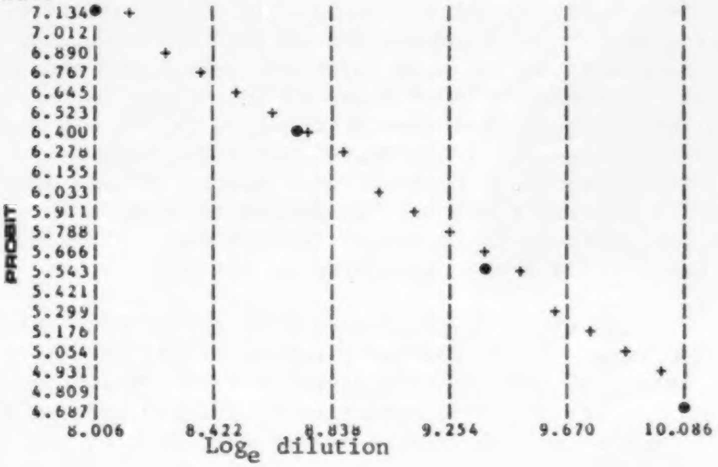

Fig. 3 - Hard copy computer print out of results for computer assisted micro-dye-uptake interferon assay of NIH - Reference Interferon.

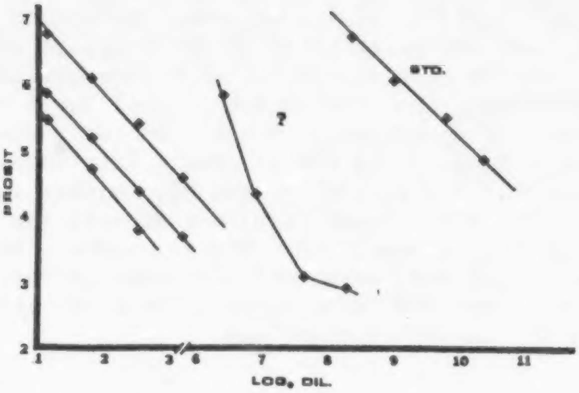

Fig. 4: Interferon assay curves generated from a single micro-assay plate, illustrating role of slope and linearity in determining possible errors in an assay. The reference interferon curve is on the far right and 4 unknown samples are on the left. The 3 samples on the far left and the standard on the right have similar slopes and are quite linear; whereas the fourth curve has a much steeper slope and is skewed. This occurrence usually indicated that something was wrong with the assay such as contamination, pipetting error, or CO_2 atmosphere blockage to the wells of the plate, and the sample was re-assayed.

The performance of this assay was assessed against the plaque reduction method. The titers obtained for over 50 assays of NIH reference interferon over a several month period by each of the assays was compared. Also, 5 assays performed over a several week period of an internal control interferon were examined. The number of assays done in this second comparison study was small; however, it illustrated how the reference correlation factor produced by the standard of each plate of assays functioned to reduce the variance in the computer assisted micro assay.

The statistics of the comparison of these control interferons are presented in Table 1. The upper set of data compares the statistics from the titers obtained for the NIH reference interferon by each method. The mean NIH reference standard titer,(19,800 u/ml), obtained by the computer assisted interferon assay (CAIA) was almost twice that obtained by the plaque reduction (PR_{50}) method, 10,300 u/ml, and was almost identical to the known titer of NIH standard, 20,000 u/ml. The standard deviation of the CAIA titers was nearly twice as large as for the PR_{50} method. This would be expected if the sensitivity of the CAIA was twice that of the PR_{50} method and the variability of the 2 assays was the same. Comparison of the coefficients of variation obtained by each assay demonstrated that the variability of the 2 methods was almost equal for uncorrected titers. On the average in these studies, 1 unit/ml of the NIH reference interferon assayed as approximately 0.5 unit/ml by the PR_{50} method and as 1 unit/ml by the CAIA. These results suggested that the CAIA was almost twice as sensitive. These studies were quite interesting since both assay methods compared here utilized the same cell line and viral strain. Both were kindly donated by Dr. Cantell 4 years ago.

NIH REFERENCE STANDARD (20,000 u/ml)

	PR_{50}	CAIA
N	58	52
$\bar{X}$	10,261 u/ml	19,761 u/ml
S.D.	± 4,777	± 8,968
C.V.	47%	45%
1 IRU	0.51 u/ml	0.988 u/ml

INTERNAL CONTROL

	UNCORRELATED	RU	UNCORRELATED	RU
N	5	5	5	5
$\bar{X}$	17,928	25,214	13,967	22,400
S.D.	± 11,477	± 17,621	± 6,195	± 3,376
C.V.	64%	70%	44%	15%

Table 1: Statistical comparison of the plaque-reduction-50 (PR_{50}) and the computer assisted micro interferon assay (CAIA) of NIH reference standard (top) and an internal control by uncorrelated and reference titers (bottom). (RU = reference units).

The second set of data in Table 1 were from the titers obtained from an internal control preparation of crude interferon. The statistics in the left hand columns, under each assay heading were based on uncorrelated titers. Those statistics in the right hand columns are based on titers for the assays after they were converted to reference units (RU). These preliminary data indicated that the standard deviation and coefficient of variation of the sample titers by the micro method could be substantially reduced by correction to reference units with a reference factor derived from the standard assayed on each plate. The variance in the micro assay for the NIH standard and the uncorrelated internal control were nearly identical, but the coefficient of variation for the titers converted to reference units was reduced almost 3-fold. This would suggest that the variance in the assay was primarily due to a difference in sensitivity from plate to plate which was corrected for by the correlation factor. However, this didn't appear to be the cause of the variation encountered with the plaque reduction assays of the internal control preparation. Here the standard deviation and coefficient of variation for uncorrelated and reference titers were higher than for the NIH reference standard assays above and these statistics increased when the internal control titers were converted to reference units. This difference between the assays could have been due to the greater degree of difficulty encountered in trying to produce the same culture conditions in all parts of the physically much larger plaque reduction assay as compared to the small microtiter assay plates.

Table 2: Additional advantages of the computer assisted micro-dye uptake interferon assay compared to the plaque reduction-50 method.

1. 33% less turnaround time - 48 hours compared to 72 hours.

2. 5.36 fold more assays/week/technician, 75 compared to 14.

3 12.7 fold less media and serum.

4. 20 fold less cells to set up assays.

5. 5.3 fold less incubator space.

6. 13.3 fold less sample volume required, 0.45 ml compared to 6 ml to do an initial dilution of 1:3.

During routine use of the micro assay over a several month period we found several other advantages in the micro assay system over the plaque reduction method besides greater sensitivity and ease of use. Some of these advantages are listed in Table 2.

CONCLUSION

The computer assisted micro-dye uptake assay procedure was efficient, economical and easy to use. The reproducibility of the assay was as good for uncorrelated titers, and substantially better for reference correlated titers than the plaque reduction method. The computer assisted assay was also found to have good sensitivity. By incorporating automated spectrophotometric reading of samples and computer processing of the data, technician variation was reduced.

However, there were also some drawbacks encountered with the system. It was difficult to determine when 90-95% CPE had occurred on the viral control without experience. This could be a source of error until familiarity with the assay is gained. The problem of the maintenance and processing of large numbers of microtiter plates can be reduced by utilizing automated cell culture procedures for the plates, and by direct interfacing of the spectrophotometer and the computer. Overall the CAIA has greatly increased the laboratory's capacity to process clinical and research interferon specimens.

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4.6.2 Quality Control Procedures

The quality control procedures used in this bioassay are briefly described below. All samples are analyzed both induced and non-induced and standard tissue QC techniques are followed for this in vitro test system. Table 4-5 summarizes the frequency, control limits and corrective action appropriate to these techniques.

A. Negative Controls (viral controls)

A negative control (virus challenged) of 8 wells is run for each group of the standard interferon preparations and 4 unknown samples. The values for these data are incorporated as the background of the assay and used in all calculations of titers. This represents 100 percent CPE.

B. Positive Controls (cell control)

Positive controls (cell control) of 8 wells are run for each group as above. This data represents the 0 percent CPE and is used in the calculation of all sample titers for that plate.

C. Reference Standards

WHO International Reference Preparation of Mouse Interferon, 12,000 IU/ml prepared by National Institute of Allergy and Infectious Diseases, NIH (catalog #G-002-904-511) is run in duplicate at 8 dilutions. It is assayed with each group of 4 unknown sample titers obtained from the reference standard and used to compute correction factor for the unknown samples to yield reference units.

D. Replicate Assays

All standards and unknown samples are run in duplicate and raw data is averaged to calculate titers.

TABLE 4-5. INTERNAL QC REQUIREMENTS - TYPE 1 INTERFERON ASSAY

Operation check	Frequency	Control limits	Corrective action planned
Negative Controls	Each group of 4 samples	85-95% CPE	Rerun standard plus samples
Positive Controls	Each group of 4 samples	Not applicable	Not applicable
Standards	Each group of 4 samples	Standard assays within half to twice its known value	Rerun standard plus samples
Replicate Assays	Every sample	Twice the variance of well to well replicates	Edit dilution from calculations Reassay sample

5.0 DATA REPORTING FORMS

5.1 OVERVIEW

Examples of each of the data reporting forms used in the Love Canal Study are provided in this section. Included for each analysis are the appropriate analyte concentration forms and internal QC forms for reporting data on spiked or known QC samples and surrogates and internal standards, as applicable. Data forms for reporting qualitative identifications by GC/MS and for making highly relevant comments on individual samples are also provided. Table 5-1 correlates each analysis with the appropriate data coding form. In this section, data forms are presented numerically. Forms J09, J10, J26 and J27 are not yet available. Coding of data on these four forms will be performed by the Prime Contractor.

Instructions for completing data reporting forms are described in a separate document, the data coding manual. This manual was provided to each contractor with the initial shipment of reporting forms.

TABLE 5-1. ANALYSIS METHOD-DATA REPORTING FORM CROSS REFERENCE

Medium	Analysis	Appendix B Section(s)	Data reporting forms
AIR:	Volatiles	1.2	J03, J13
	Pesticides	1.3	J02, J12
	Metals	1.4	J07, J14
	Dioxins	1.5	J10, J27
WATER:	Volatiles	2.2	J04, J15, J16
	Semivolatiles	2.3	J05, J17, J18
	Pesticides	2.4	J06, J19
	Metals	2.5	J07, J14
	Anions	2.6	J08, J20
	TOC	2.7	J09, J26
	TOX	2.8	J09, J26
	Dioxins	2.9	J10, J27
SOIL/SEDIMENT:	Volatiles	3.2	J04, J21, J22
	Semivolatiles	3.3	J05, J23, J24
	Pesticides	3.4	J06, J25
	Metals	3.5	J07, J14
	Dioxins	3.6	J10, J27
BIOTA:	Volatiles	4.2	J04
	Semivolatiles	4.2	J05
	Pesticides	4.2	J06

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

				DATE	TIME	SAMPLE
SAMPLE ID	MEDIUM	METHOD	LAB. ID	MO. DA.	HR. MN.	SIZE

ANALYTE CONCENTRATION

POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE	CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE		SEQ. NO.
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	
									A	1	

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

PESTICIDES AND RELATED COMPOUNDS ON POLYURETHANE FOAM PLUGS

	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
LINDANE	F01								A 1	0 0 1
HEXACHLOROBENZENE	F02								A 1	0 0 2
HEXACHLOROCYCLOPENTADIENE	F03								A 1	0 0 3
1,2,3,4-TETRACHLOROBENZENE	F04								A 1	0 0 4
1,2,3-TRICHLOROBENZENE	F05								A 1	0 0 5
1,2,4-TRICHLOROBENZENE	F06								A 1	0 0 6
1,3,5-TRICHLOROBENZENE	F07								A 1	0 0 7
2,4,5-TRICHLOROPHENOL	F08								A 1	0 0 8
PENTACHLOROBENZENE	F09								A 1	0 0 9
HEXACHLORO-1,3-BUTADIENE	F11								A 1	0 1 1
1,2,4,5-TETRACHLOROBENZENE	F12								A 1	0 1 2
A,A,2,6-TETRACHLOROTOLUENE	F13								A 1	0 1 3
PENTACHLORO-1,3-BUTADIENE	F14								A 1	0 1 4
PENTACHLORONIzROBENZENE	F15								A 1	0 1 5
1,2,3,5-TETRACHLOROBENZENE	F16								A 1	0 1 6
A-BENZENEHEXACHLORIDE (A-BHC)	F17								A 1	0 1 7
HEPTACHLOR	F18								A 1	0 1 8
									A 1	

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

VOLATILE ORGANICS ON TENAX

	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
BENZENE	T01							▨	A1	001
CARBON TETRACHLORIDE	T02							▨	A1	002
CHLOROBENZENE	T03							▨	A1	003
O-CHLOROTOLUENE	T04							▨	A1	004
P-CHLOROTOLUENE	T05							▨	A1	005
1,2-DIBROMOETHANE	T06							▨	A1	006
O-DICHLOROBENZENE	T07							▨	A1	007
P-DICHLOROBENZENE	T08							▨	A1	008
1,1,2,2-TETRACHLOROETHYLENE	T09							▨	A1	009
TOLUENE	T10							▨	A1	010
1,2,3-TRICHLOROBENZNE	T11							▨	A1	011
1,2,4-TRICHLOROBENZENE	T12							▨	A1	012
1,3,5-TRICHLOROBENZENE	T13							▨	A1	013
CHLOROFORM	T14	▨						▨	A1	014
1,2-DICHLOROETHANE	T15	▨						▨	A1	015
2,4-DICHLOROTOLUENE	T16	▨						▨	A1	016
O-CHLOROBENZALDEHYDE	T17	▨						▨	A1	017
P-CHLOROBENZALDEHYDE	T18	▨						▨	A1	018
BENZYL CHLORIDE (A-CHLOROTOLUENE)	T19	▨						▨	A1	019

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

VOLATILE ORGANICS ON TENAX

1,1-DICHLOROETHANE
1,1-DICHLOROETHYLENE (VINYLIDENE CH)
1,2-DICHLOROETHYLENE
DICHLOROMETHANE
PHENOL
O-XYLENE
M-XYLENE
P-XYLENE

POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
T20								A1	020
T21								A1	021
T22								A1	022
T23								A1	023
T24								A1	024
T25								A1	025
T26								A1	026
T27								A1	027
								A1	
								A1	
								A1	
								A1	
								A1	
								A1	
								A1	
								A1	
								A1	
								A1	
								A1	

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

VOLATILE ORGANICS IN WATER, SOIL, SEDIMENT, BIOTA

	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE	CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
METHYLENE CHLORIDE	V01									A 1	001
CHLOROMETHANE	V02									A 1	002
1,1-DICHLOROETHENE	V03									A 1	003
BROMOMETHANE	V04									A 1	004
1,1-DICHLOROETHANE	V05									A 1	005
VINYL CHLORIDE	V06									A 1	006
CIS-1,2-DICHLOROETHENE	V07									A 1	007
CHLOROETHANE	V08									A 1	008
TRANS-1,2-DICHLOROETHENE	V09									A 1	009
TRICHLOROFLUOROMETHANE	V10									A 1	010
CHLOROFORM	V11									A 1	011
1,2-DICHLOROETHANE	V12									A 1	012
1,1,1-TRICHLOROETHANE	V14									A 1	014
CARBON TETRACHLORIDE	V15									A 1	015
BROMOCHLOROMETHANE	V16									A 1	016
BROMODICHLOROMETHANE	V17									A 1	017
2,3-DICHLOROPROPENE-1	V18									A 1	018
1,2-DICHLOROPROPANE	V19									A 1	019

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

VOLATILE ORGANICS IN WATER, SOIL, SEDIMENT, BIOTA

	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
TRICHLOROETHENE	V20								A1	020
TRANS-1,3-DICHLOROPROPENE	V21								A1	021
BENZENE	V22								A1	022
ACROLEIN	V23								A1	023
ACRYLONITRILE	V24								A1	024
DIBROMOCHLOROMETHANE	V25								A1	025
1,1,2-TRICHLOROETHANE	V26								A1	026
BROMOFORM	V27								A1	027
1,1,2,2-TETRACHLOROETHANE	V28								A1	028
BENZYL CHLORIDE	V29								A1	029
O-XYLENE	V30								A1	030
M-XYLENE	V31								A1	031
P-XYLENE	V32								A1	032
TETRACHLOROETHENE	V33								A1	033
TOLUENE	V34								A1	034
2-CHLOROTOLUENE	V35								A1	035
3-CHLOROTOLUENE	V36								A1	036
4-CHLOROTOLUENE	V37								A1	037
CHLOROBENZENE	V38								A1	038

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

VOLATILE ORGANICS IN WATER, SOIL, SEDIMENT, BIOTA

ETHYL BENZENE

1,2-DIBROMOETHANE

POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
V39								A 1	039
V40								A 1	040
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	
								A 1	

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

SEMIVOLATILE ORGANICS IN WATER, SOIL, SEDIMENT, BIOTA	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
2-CHLOROPHENOL	A01								A1	001
3-CHLOROPHENOL	A02								A1	002
4-CHLOROPHENOL	A03								A1	003
2-NITROPHENOL	A04								A1	004
PHENOL	A05								A1	005
2,4-DIMETHYLPHENOL	A06								A1	006
2,4-DICHLOROPHENOL	A07								A1	007
2,3,6-TRICHLOROPHENOL	A08								A1	008
2,4,6-TRICHLOROPHENOL	A09								A1	009
4-CHLORO-3-METHYLPHENOL	A10								A1	010
2,4-DINITROPHENOL	A11								A1	011
2-METHYL-4,6-DINITROPHENOL	A12								A1	012
PENTACHLOROPHENOL	A13								A1	013
4-NITROPHENOL	A14								A1	014
HEXACHLOROETHANE	B01								A1	015
1,4-DICHLOROBENZENE	B02								A1	016
1,3-DICHLOROBENZENE	B03								A1	017
1,2-DICHLOROBENZENE	B04								A1	018
BIS(2-CHLOROETHYL)ETHER	B05								A1	019

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

SEMIVOLATILE ORGANICS IN WATER, SOIL, SEDIMENT, BIOTA

	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
BIS(2-CHLOROISOROPYL)ETHER	B06								A 1	020
N-NITROSODI-N-PROPYLAMINE	B07								A 1	021
HEXACHLOROBUTADIENE	B08								A 1	022
1,2,3-TRICHLOROBENZENE	B09								A 1	023
N-NITROSODIMETHYLAMINE	B10								A 1	024
1,2,4-TRICHLOROBENZENE	B11								A 1	025
1,3,5-TRICHLOROBENZENE	B12								A 1	026
NITROBENZENE	B13								A 1	027
NAPHTHALENE	B14								A 1	028
ISOPHORONE	B15								A 1	029
BIS(2-CHLOROETHOXY)METHANE	B16								A 1	030
HEXACHLOROCYCLOPENTADIENE	B17								A 1	031
2-CHLORONAPHTHALENE	B18								A 1	032
ACENAPHTYLENE	B19								A 1	033
ACENAPHTHENE	B20								A 1	034
DIMETHYLPHTHALATE	B21								A 1	035
2,6-DINITROTOLUENE	B22								A 1	036
FLUORENE	B23								A 1	037
1,2-DIPHENYLHYDRAZINE	B24								A 1	038

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

SEMIVOLATILE ORGANICS IN WATER, SOIL, SEDIMENT, BIOTA	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
4-CHLOROPHENYLPHENYL ETHER	B25								A1	039
2,4-DINITROTOLUENE	B26								A1	040
2,4-DICHLOROTOLUENE	B27								A1	041
DIETHYLPHTHALATE	B28								A1	042
N-NITROSODIPHENYLAMINE	B29								A1	043
HEXACHLOROBENZENE	B30								A1	044
4-BROMOPHENYLPHENYLETHER	B31								A1	045
PHENANTHRENE	B32								A1	046
ANTHRACENE	B33								A1	047
DI-N-BUTYL PHTHALATE	B34								A1	048
FLUORANTHENE	B35								A1	049
PYRENE	B36								A1	050
BENZIDINE	B37								A1	051
BUTYLBENZYLPHTHALATE	B38								A1	052
DI(2-ETHYLHEXYL)PHTHALATE	B39								A1	053
CHRYSENE	B40								A1	054
DI-N-OCTYLPHTHALATE	B41								A1	055
BENZO(A)ANTHRACENE	B42								A1	056
BENZO(K)FLUORANTHENE	B43								A1	057

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

SEMIVOLATILE ORGANICS IN WATER, SOIL, SEDIMENT, BIOTA

	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE	CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
BENZO(B) FLUORANTHENE	B44									A1	058
BENZO(A)PYRENE	B45									A1	059
3,3-DICHLOROBENZIDINE	B46									A1	060
INDENO(1,2,3-CD)PYRENE	B47									A1	061
DIBENZO(A,H)ANTHRACENE	B48									A1	062
BENZO(G,H,I)PERYLENE	B49									A1	063
PENTACHLORONITROBENZENE	B50									A1	064
2,4,6-TRICHLOROANILINE	B51									A1	065
4-CHLOROBENZOTRIFLUORIDE (TRIFLUORO)	B52									A1	066
1,2,3,4-TETRACHLOROBENZENE	B53									A1	067
1,2,4,5-TETRACHLOROBENZENE	B54									A1	068
	B56									A1	070
										A1	
										A1	
										A1	
										A1	
										A1	
										A1	

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LC 1-619-026-☐☐-J06-☐☐☐☐☐-1

LOVE CANAL MONITORING PROJECT

COMPLETED BY: ____________

ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

PESTICIDES IN WATER, SOIL, SEDIMENT, BIOTA

	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
ALPHA-BHC	P01								A 1	0 0 1
BETA-BHC	P02								A 1	0 0 2
GAMMA-BHC	P03								A 1	0 0 3
DELTA-BHC	P04								A 1	0 0 4
HEPTACHLOR	P05								A 1	0 0 5
ALDRIN	P06								A 1	0 0 6
MIREX	P07								A 1	0 0 7
ENDOSULFAN I	P08								A 1	0 0 8
HEPTACHLOR EPOXIDE	P09								A 1	0 0 9
DDE	P10								A 1	0 1 0
ENDRIN	P11								A 1	0 1 1
ENDOSULFAN II	P12								A 1	0 1 2
DIELDRIN	P13								A 1	0 1 3
ENDOSULFAN SULFATE	P14								A 1	0 1 4
DDD	P15								A 1	0 1 5
CHLORDANE	P16								A 1	0 1 6
DDT	P17								A 1	0 1 7
TOXAPHENE	P18								A 1	0 1 8
AROCLOR 1221	P19								A 1	0 1 9

8/80

LC 1-619-026-☐☐-J06-☐☐☐☐☐-2

LOVE CANAL MONITORING PROJECT

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

PESTICIDES IN WATER, SOIL, SEDIMENT, BIOTA

	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE	CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
AROCLOR 1254	P20									A 1	020
AROCLOR 1016	P21									A 1	021
AROCLOR 1232	P22									A 1	022
AROCLOR 1242	P23									A 1	023
AROCLOR 1248	P24									A 1	024
AROCLOR 1260	P25									A 1	025
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	

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ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

METALS IN AIR, WATER, SOIL, SEDIMENT

	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
ANTIMONY	101								A1	001
ARSENIC	102								A1	002
BARIUM	103								A1	003
BERYLLIUM	104								A1	004
CADMIUM	105								A1	005
CHROMIUM	106								A1	006
COPPER	107								A1	007
LEAD	108								A1	008
NICKEL	109								A1	009
MERCURY	110								A1	010
SELENIUM	111								A1	011
SILVER	112								A1	012
THALLIUM	113								A1	013
ZINC	114								A1	014
									A1	
									A1	
									A1	
									A1	
									A1	

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COMPLETED BY: ____________

ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
		ANION	▨			▲

ANIONS IN WATER

FLUORIDE

NITRATE

POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	TRACE	QUALITATIVE CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
115							▨	A1	001
116							▨	A1	002
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	
							▨	A1	

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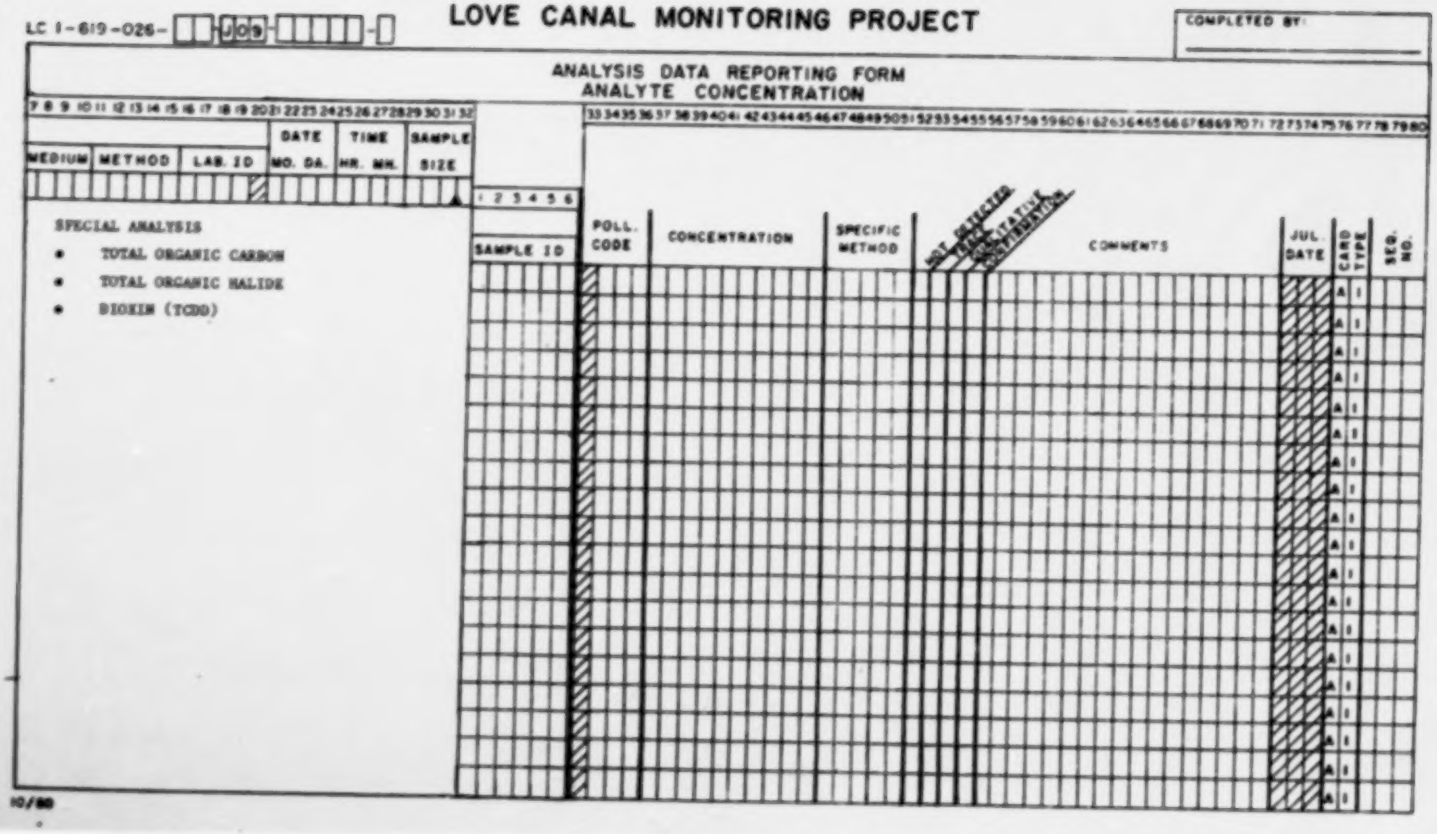

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LOVE CANAL MONITORING PROJECT

COMPLETED BY:

ANALYSIS DATA REPORTING FORM
ANALYTE CONCENTRATION

7 8 9	10 11 12 13 14 15 16 17 18 19	20 21 22 23	24 25 26 27	28 29 30 31 32
		DATE	TIME	SAMPLE
MEDIUM	METHOD / LAB. ID	MO. DA.	HR. MN.	SIZE

SPECIAL ANALYSIS

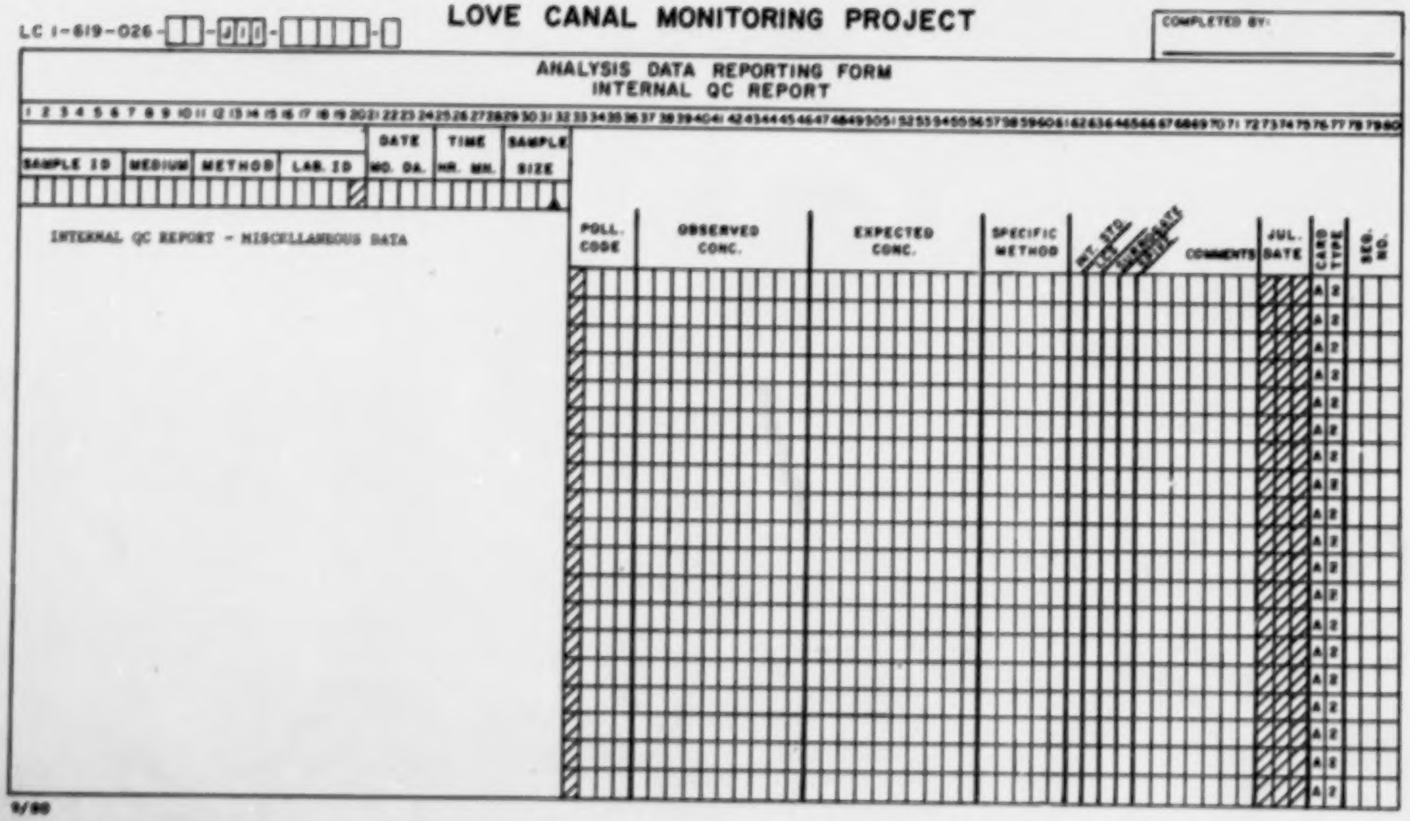
- TOTAL ORGANIC CARBON
- TOTAL ORGANIC HALIDE
- DIOXIN (TCDD)

1 2 3 4 5 6

33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	POLL. CODE	CONCENTRATION	SPECIFIC METHOD	NOT DETECTED	[illegible]	QUALITATIVE	CONFIRMATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	
										A 1	

10/80



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LOVE CANAL MONITORING PROJECT

COMPLETED BY:

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

INTERNAL QC REPORT - MISCELLANEOUS DATA

POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD.		COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	

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COMPLETED BY: ____________

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
Q0	AIR					

POLYURETHANE FOAM PLUGS - QC DATA
- LABORATORY CONTROL STANDARD
- SPIKED SAMPLE

	POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD. LCS SURROGATE SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
LINDANE	S01							A2	001
HEXACHLOROBENZENE	S02							A2	002
HEXACHLOROCYCLOPENTADIENE	S03							A2	003
1,2,3,4-TETRACHLOROBENZENE	S04							A2	004
2,4,5-TRICHLOROPHENOL	S05							A2	005
PENTACHLOROBENZENE	S06							A2	006
1,2,3-TRICHLOROBENZENE	S22							A2	007
1,2,4-TRICHLOROBENZENE	S39							A2	008
1,3,5-TRICHLOROBENZENE	S31							A2	009
								A2	
								A2	
								A2	
								A2	
								A2	
								A2	
								A2	
								A2	
								A2	
								A2	

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COMPLETED BY:

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

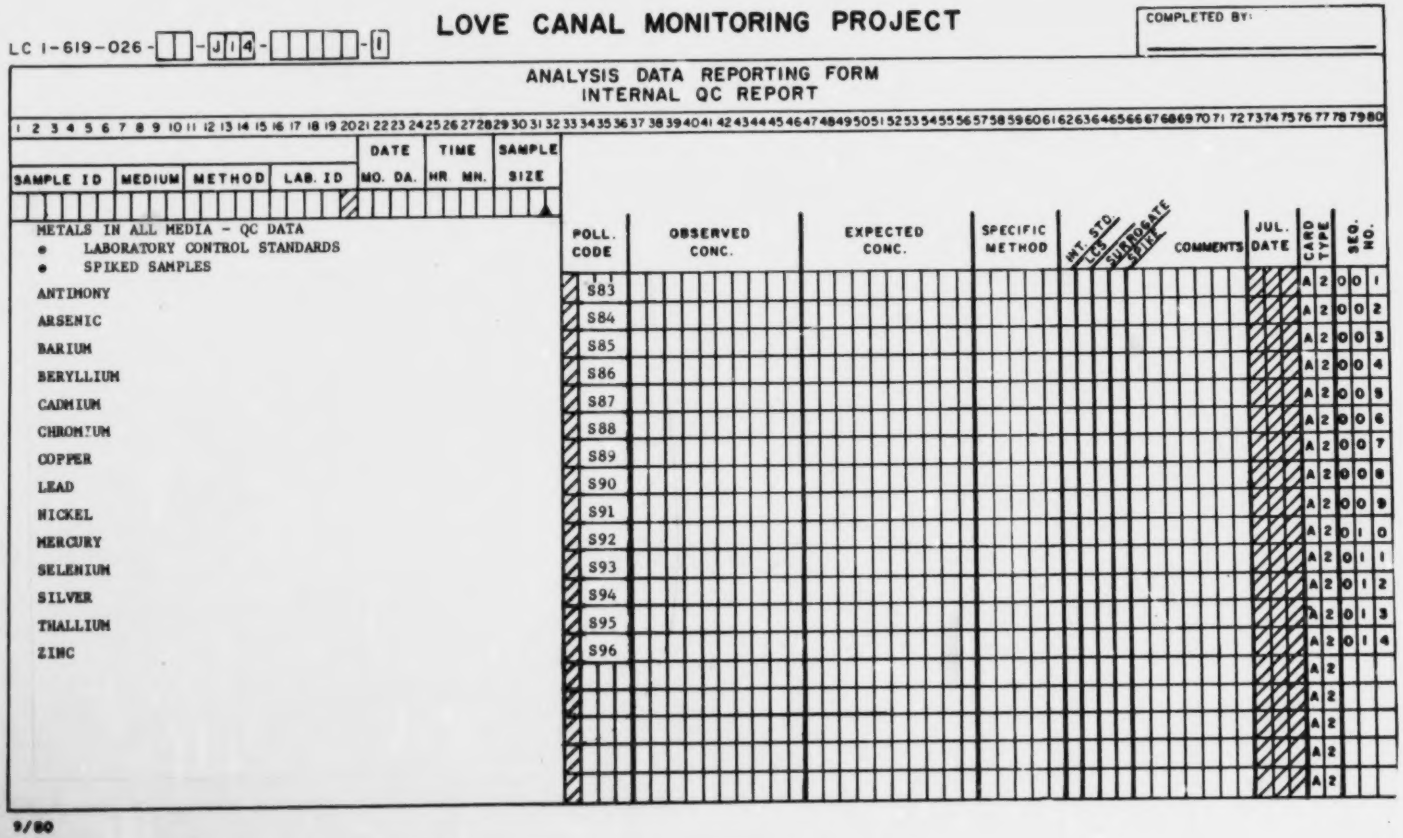
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
	AIR					

TENAX CARTRIDGES - QC DATA
- LABORATORY CONTROL STANDARD

	POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD.	LCS	SURROGATE SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
BENZENE	S07									A2	001
CARBON TETRACHLORIDE	S08									A2	002
CHLOROBENZENE	S09									A2	003
O-CHLOROTOLUENE	S10									A2	004
P-CHLOROTOLUENE	S11									A2	005
1,2-DIBROMOETHANE	S12									A2	006
O-DICHLOROBENZENE	S13									A2	007
P-DICHLOROBENZENE	S14									A2	008
1,1,2,2-TETRACHLOROETHYLENE	S15									A2	009
TOLUENE	S16									A2	010
1,2,3-TRICHLOROBENZENE	S22									A2	011
1,2,4-TRICHLOROBENZENE	S39									A2	012
1,3,5-TRICHLOROBENZENE	S31									A2	013
										A2	
										A2	
										A2	
										A2	
										A2	
										A2	

9/80



LC 1-619-026-☐☐-J14-☐☐☐☐☐-1

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ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR MN.	SAMPLE SIZE

METALS IN ALL MEDIA - QC DATA
- LABORATORY CONTROL STANDARDS
- SPIKED SAMPLES

	POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD.	LCS	SURROGATE SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
ANTIMONY	S83									A2	001
ARSENIC	S84									A2	002
BARIUM	S85									A2	003
BERYLLIUM	S86									A2	004
CADMIUM	S87									A2	005
CHROMIUM	S88									A2	006
COPPER	S89									A2	007
LEAD	S90									A2	008
NICKEL	S91									A2	009
MERCURY	S92									A2	010
SELENIUM	S93									A2	011
SILVER	S94									A2	012
THALLIUM	S95									A2	013
ZINC	S96									A2	014
										A2	
										A2	
										A2	
										A2	
										A2	

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LC 1-619-026-☐☐-J15-☐☐☐☐☐-1

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ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
0 0	H 2 0					

VOLATILE ORGANICS IN WATER - QC DATA
- LABORATORY CONTROL STANDARD
- SPIKED SAMPLE

	POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD	LCS	SURROGATE SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
BENZENE	S07									A 2	0 0 1
CHLOROFORM	S23									A 2	0 0 2
BROMOFORM	S24									A 2	0 0 3
SYM-TETRACHLOROETHANE	S25									A 2	0 0 4
P-BROMOFLUOROBENZENE	S26									A 2	0 0 5
CARBON TETRACHLORIDE	S27									A 2	0 0 6
FLUOROBENZENE	S28									A 2	0 0 7
TRICHLOROETHYLENE	S29									A 2	0 0 8
TETRACHLOROETHYLENE	S30									A 2	0 0 9
CHLOROBENZENE	S09									A 2	0 1 0
ACROLEIN	S59									A 2	0 1 1
ACRYLONITRILE	S60									A 2	0 1 2
										A 2	
										A 2	
										A 2	
										A 2	
										A 2	
										A 2	
										A 2	

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LC 1-619-026-☐☐-J16-☐☐☐☐☐-1

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ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
	H2O					

VOLATILE ORGANICS IN WATER - QC DATA
- SURROGATES
- INTERNAL STANDARDS

	POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD	LCS	SURROGATE SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
FLUOROBENZENE	S17									A2	001
P-BROMOFLUOROBENZENE	S18									A2	002
1,4-DIFLUOROBENZENE	S19									A2	003
PENTAFLUOROBENZENE	S20									A2	004
2-BROMO-1-CHLOROPROPANE	S21									A2	005
										A2	
										A2	
										A2	
										A2	
										A2	
										A2	
										A2	
										A2	
										A2	
										A2	
										A2	
										A2	
										A2	
										A2	

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LOVE CANAL MONITORING PROJECT

COMPLETED BY: ____________

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
QO	H2O					

SEMIVOLATILE ORGANICS IN WATER - QC DATA
- LABORATORY CONTROL STANDARD
- SPIKED SAMPLE

	POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD.	LCS	SURROGATE SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
1,4-DICHLOROBENZENE	S38									A2	001
1,2,4-TRICHLOROBENZENE	S39									A2	002
1,2,3,4-TETRACHLOROBENZENE	S40									A2	003
FLUORANTHENE	S41									A2	004
2,4,6-TRICHLOROPHENOL	S42									A2	005
2-CHLORONAPHTHALENE	S43									A2	006
2,6-DINITROTOLUENE	S44									A2	007
4-NITROPHENOL	S45									A2	008
2-FLUOROPHENOL	S46									A2	009
PENTACHLOROPHENOL	S47									A2	010
BETA-BENZENEHEXACHLORIDE	S48									A2	011
1-FLUORONAPHTHALENE	S49									A2	012
4,4-DIBROMOBIPHENYL	S50									A2	013
4,4-DIBROMOOCTAFLUOROBIPHENYL	S51									A2	014
DI-M-BUTYLPHTHALATE	S52									A2	015
BENZIDINE	S61									A2	016
HEXACHLOROCYCLOPENTADIENE	S03									A2	017
										A2	
										A2	

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LC 1-619-026-☐☐-J18-☐☐☐☐☐-1

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COMPLETED BY: ____________

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
Q 0	H 2 0					

SEMIVOLATILE ORGANICS IN WATER - QC DATA
- SURROGATES
- INTERNAL STANDARDS

2-FLUOROPHENOL

1-FLUORONAPHTHALENE

4,4(PRIME)-DIBROMOOCTAFLUOROBIPHENYL

ANTHRACENE-D SUB 10

NAPHTHALENE-D SUB 8

CHRYSENE-D SUB 12

POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD	LCS	SURROGATE SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
S32									A 2	0 0 1
S33									A 2	0 0 2
S34									A 2	0 0 3
S35									A 2	0 0 4
S36									A 2	0 0 5
S37									A 2	0 0 6
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	

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LC 1-619-026-☐☐-J19-☐☐☐☐☐-1

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COMPLETED BY: ____________

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
QO	H2O					

PESTICIDES IN WATER - QC DATA
- LABORATORY CONTROL STANDARDS
- SPIKED SAMPLE

AROCLOR 1242

POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD.	LCS	SURROGATE SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
S99									A2	001
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	
									A2	

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COMPLETED BY: ______________

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
Q0	H2O	ANION				

ANIONS IN WATER - QC DATA
- LABORATORY CONTROL STANDARD
- SPIKED SAMPLE

FLUORIDE

NITRATE

POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD. / LCS / SURROGATE / SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
S97							A2	001
S98							A2	002
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	
							A2	

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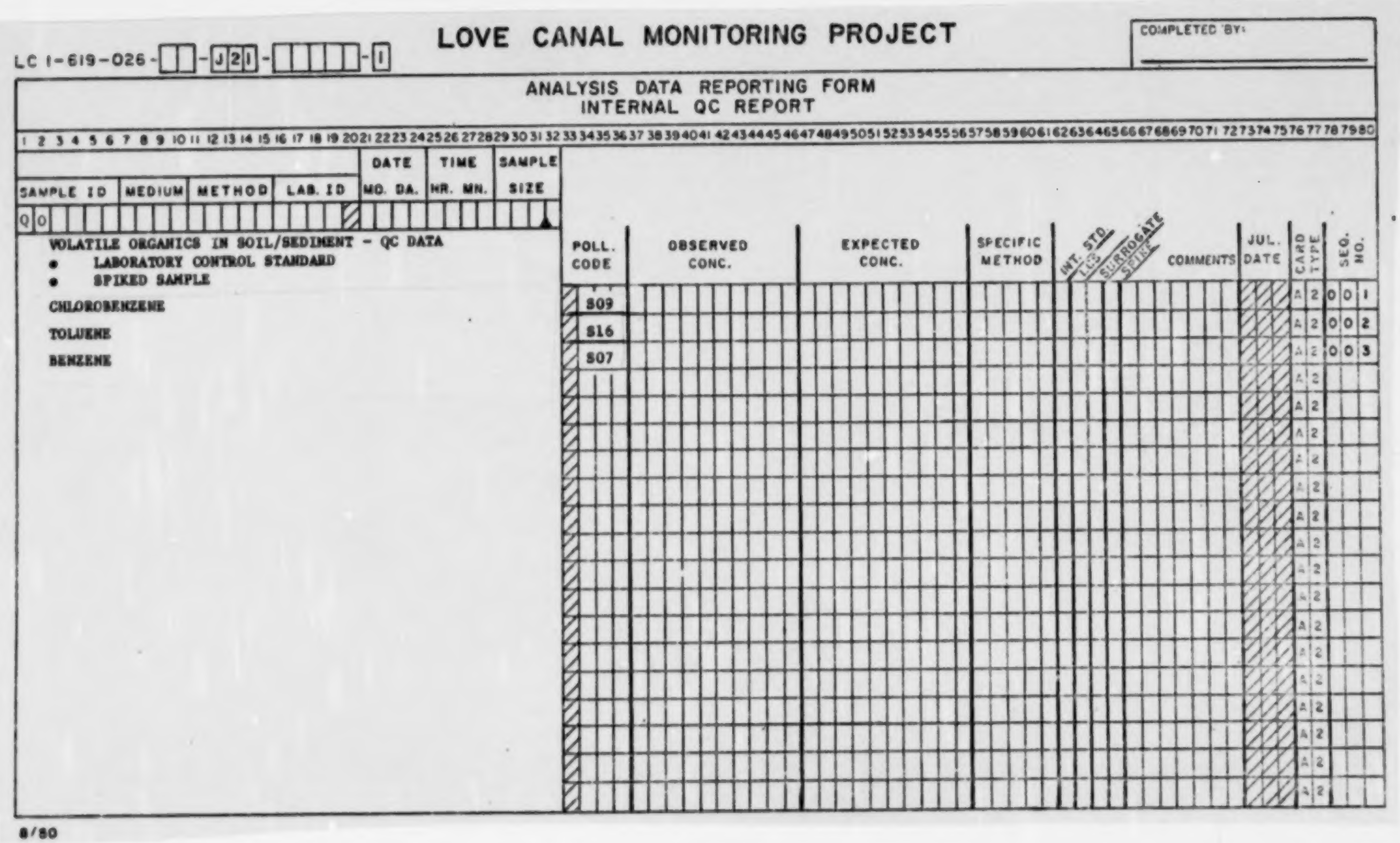

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LOVE CANAL MONITORING PROJECT

COMPLETED BY:

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
Q0						

VOLATILE ORGANICS IN SOIL/SEDIMENT - QC DATA
- LABORATORY CONTROL STANDARD
- SPIKED SAMPLE

	POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD.	LCS	SURROGATE	SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
CHLOROBENZENE	809										A2	001
TOLUENE	816										A2	002
BENZENE	807										A2	003
											A2	
											A2	
											A2	
											A2	
											A2	
											A2	
											A2	
											A2	
											A2	
											A2	
											A2	
											A2	
											A2	
											A2	
											A2	
											A2	

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LC 1-619-026-☐☐-J22-☐☐☐☐☐-1

LOVE CANAL MONITORING PROJECT

COMPLETED BY: ____________

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

VOLATILE ORGANICS IN SOIL/SEDIMENT - QC DATA
- SURROGATES
- INTERNAL STANDARDS

1,2-DICHLOROETHANE-D SUB 4
CARBON TETRACHLORIDE-13 C 1
P-CHLOROTOLUENE-D SUB 4
DICHLOROMETHANE-D SUB 2
TOLUENE-D SUB 8
BENZENE-D SUB 6

POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD.	LCS	SURROGATE SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
S53									A 2	0 0 1
S54									A 2	0 0 2
S55									A 2	0 0 3
S56									A 2	0 0 4
S57									A 2	0 0 5
S58									A 2	0 0 6
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	
									A 2	

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LOVE CANAL MONITORING PROJECT

COMPLETED BY:

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
0 0						

SEMIVOLATILE ORGANICS IN SOIL/SEDIMENT - QC DATA

- LABORATORY CONTROL STANDARD
- SPIKED SAMPLE

	POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD / LCS / SURROGATE SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
1,2,4-TRICHLOROBENZENE	S70							A 2	0 0 1
2,4-DINITROTOLUENE	S71							A 2	0 0 2
DI-N-BUTYL-PHTHALATE	S72							A 2	0 0 3
PYRENE	S73							A 2	0 0 4
N-NITROSO-DI-N-PROPYLAMINE	S74							A 2	0 0 5
1,4-DICHLOROBENZENE	S75							A 2	0 0 6
PENTACHLOROPHENOL	S76							A 2	0 0 7
2-CHLOROPHENOL	S77							A 2	0 0 8
P-CHLORO-M-CRESOL	S78							A 2	0 0 9
4-NITROPHENOL	S79							A 2	0 1 0
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	
								A 2	

8/80

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LOVE CANAL MONITORING PROJECT

COMPLETED BY: ____________

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE

SEMIVOLATILE ORGANICS IN SOIL/SEDIMENT - QC DATA
- SURROGATES
- INTERNAL STANDARDS

	POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD. / LCS / SURROGATE SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
HEXACHLOROBENZENE-13 C 6	S62							A2	001
PENTACHLOROPHENOL-13 C 6	S63							A2	002
2-CHLOROPHENOL-13 C 6	S64							A2	003
TETRACHLOROBENZENE-13 C 6	S65							A2	004
P-CHLOROTOLUENE-D SUB 4	S66							A2	005
NAPHTHALENE-D SUB 8	S67							A2	006
ANTHRACENE-D SUB 10	S68							A2	007
CHRYSENE-D SUB 12	S69							A2	008
								A2	
								A2	
								A2	
								A2	
								A2	
								A2	
								A2	
								A2	
								A2	
								A2	
								A2	

9/80

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LOVE CANAL MONITORING PROJECT

COMPLETED BY: ____________

ANALYSIS DATA REPORTING FORM
INTERNAL QC REPORT

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO. DA.	TIME HR. MN.	SAMPLE SIZE
0 0						

PESTICIDES IN SOIL/SEDIMENT - QC DATA
- LABORATORY CONTROL STANDARD
- SPIKED SAMPLE

	POLL. CODE	OBSERVED CONC.	EXPECTED CONC.	SPECIFIC METHOD	INT. STD.	LCS	SURROGATE	SPIKE	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
HEPTACHLOR	S80										A 2	0 0 1
ALDRIN	S81										A 2	0 0 2
DIELDRIN	S82										A 2	0 0 3
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	
											A 2	

8/80

LC 1-619-026-☐☐-J31-☐☐☐☐☐-☐

LOVE CANAL MONITORING PROJECT

COMPLETED BY: ____________

ANALYSIS DATA REPORTING FORM
QUALITATIVE ANALYSIS

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

				DATE	TIME	SAMPLE
SAMPLE ID	MEDIUM	METHOD	LAB. ID	MO. DA.	HR. MN.	SIZE

SEMIVOLATILE ORGANICS BY GC/MS
QUALITATIVE IDENTIFICATIONS

POLL. CODE		CAS #	MATCH SCORE	JUDGMENT VERIFICATION	COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	
							A 3	

9/80

LC 1-619-026- ☐☐-J41-☐☐☐☐-☐

LOVE CANAL MONITORING PROJECT

COMPLETED BY:

ANALYSIS DATA REPORTING FORM
COMMENTS

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80

SAMPLE ID	MEDIUM	METHOD	LAB. ID	DATE MO.	DATE DA.	TIME HR.	TIME MN.	SAMPLE SIZE

COMMENTS

COMMENTS	JUL. DATE	CARD TYPE	SEQ. NO.
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	
		A 4	

8/80

6.0 DOCUMENT CONTROL/CHAIN-OF-CUSTODY PROCEDURES

6.1 DOCUMENT CONTROL PROCEDURES

The purpose of document control is to ensure that all project documents will be accounted for when the project is complete. Table 6-1 lists the principal items subject to document control with records maintained by the person listed as Document Control Officer (DCO) for that document. Table 6-2 gives a more complete listing of documents generated during the project. GCA will provide a DCO onsite at the Sample Bank who will maintain overall document control for all items passing through the Sample Bank; GCA's QA Manager is the DCO overseeing document control for the entire project.

Each subcontractor shall identify a DCO for its operations who will be responsible for issuing, controlling and maintaining records of controlled documents. At the conclusion of subcontract activity, all controlled documents with records shall be provided to GCA for inclusion in an overall project document inventory.

Procedures described in Section IX of "Enforcement Considerations for Evaluations of Uncontrolled Hazardous Waste Disposal Sites by Contractors," Environmental Protection Agency, National Enforcement Investigations Center, Denver, Colorado, April 1980, shall be followed.

6.1.1 QA Project Plan

Each page will contain a heading on the upper right-hand corner that indicates Section Number, Revision Number, and Page Number of Total Pages in the section. The appropriate document numbering for subcontractor QA Plans is included with subcontract transmittal letter. When a revision to a QA Plan is made, the Table of Contents will be retyped to show the most current revision of each section, and both the revision and the revised Table of Contents will be distributed to all recipients of the original QA Plan. These recipients will be listed at the end of the QA Plan Table of Contents and in the QA Manager's records.

6.1.2 Project Numbering System

A. Project Code

The project code for the Love Canal Study is LC 1-619-026; this number must appear on sample identification tags, custody records, logbooks, data sheets, control charts, project memos and reports, document control logs, corrective action forms and logs, QA Plans, and all other project records.

TABLE 6-1. DOCUMENT CONTROL REQUIREMENTS

Item	Issued by	Numbering	Interim responsibility	DCO
Sample Collection Tags	Sample Bank	Preserialized	Sampling Subcontractor	GCA Sample Bank
Custody Records	Sample Bank	Preserialized	See Section 6.2	See Section 6.2
Field Logbooks	Sample Bank	LC 1-619-026-	Sampling Subcontractor	Sampling Subcontractor
Field Data Sheets	Sample Bank	LC 1-619-026-	Sampling Subcontractor	GCA Sample Bank
Written Communication	Various People	Number and page of personal notebook where item is cited	Recipient	Subcontractor
Photos or Drawings	Originator		Originator	Subcontractor
Analytical Sample Tags	Sample Bank	Preserialized	Shipper	Analytical Subcontractor
Laboratory Notebooks	Subcontractor	LC 1-619-026-	Analytical Subcontractor	Analytical Subcontractor
Analytical Data Sheets	GCA	LC 1-619-026-	Analytical Subcontractor	Analytical Subcontractor
QA Project Plan	GCA	Section, Revision, Page Number of Total Pages	GCA QA Manager	GCA QA Manager
QA Project Plans	Subcontractors		Subcontractors	

TABLE 6-2. SUGGESTED DOCUMENT CODES

Document	Code Letter
Project Work Plans	A
Project Logbooks	B
Sampling Logbooks	C
Sampling Data Sheets	D1, D2 etc.
Sampling Coding Form	E
Laboratory Notebooks	G
Laboratory Data Sheets	H1, H2 etc.
Laboratory Coding Form	J1, J2 etc.
Sample Logs	L1, L2 etc.
Internal Memos	M
External Written Communication	N
Confidential Information	O
Photos, Maps, Drawings	P
QA Plan	Q
Reports	R
Final Report	FR
Miscellaneous	X

B. Preserialized Documents

Sample collection and analytical tags, and custody records have preprinted serial numbers on them. It is not necessary that a tag number match a custody record number; it is necessary that each subcontractor DCO maintain records which account for all serially numbered items received. If tags or custody records are damaged, lost or destroyed before use for their intended purpose, the serial number of the item and its disposition must be recorded.

C. Other Documents

Sample identification tags and custody records are accounted for by their preserialized numbers. Other documents use the following numbering scheme to enable unique identification of each item:

Project Code	Subcontractor Code	Document Code	Serial Number
LC 1-619-026-	-00-	-A-	-00001

Table 6-2 presents a suggested document code. Each subcontractor's DCO will finalize the system to be used for their documents; it is desirable that consistent document codes be used by all subcontractors to facilitate compiling the overall project document inventory.

6.2 CHAIN-OF-CUSTODY PROCEDURES

The procedures identified here have been established for this project by the GCA QA Manager working with NEIC staff members and following guidelines developed from the following two publications:

- NEIC Policies and Procedures Manual, EPA-330/9-78-001R, Section II.

- Enforcement Considerations for Evaluations of Uncontrolled Hazardous Waste Disposal Sites by Contractors, NEIC, April 1980, Sections VIII and IX.

The purpose of chain-of-custody procedures is to document the identity of the sample, and its handling, from its first existence as a sample until its ultimate disposal. It must be possible, via a custody record, to trace a sample through all transfers of custody and to verify that it is the same sample collected.

In order to establish that a sample is valid, it is also necessary to document that no tampering has occurred - either to the sample itself, the sampling equipment used or the environment sampled. This is done by the use of evidence tape, locks and custody seals, and documented entries noting their condition in field and laboratory log books. The custody record must also document any tampering that occurred; the absence of any such comments indicates no tampering during the period of custody.

The GCA Sample Bank will provide and dispense evidence tape, sample tags, custody records, logbooks, field and laboratory data sheets, custody seals and locks as appropriate. Custody procedures are presented here in considerable detail so that they may be uniformly followed.

The sampling subcontractor shall identify an onsite person responsible for ensuring that custody procedures are followed and for referring any tampering cases or other questions to GCA's onsite QA coordinator who is responsible for onsite custody procedures. Analytical subcontractors shall also identify a person responsible for custody matters.

6.2.1 Sample Identification

Sample collection tags have been designed for air, water, soil and sediment, and biota or other samples. They are a different color for each media. The tags are preprinted to ensure that the required information is provided on each tag. Each collected sample, including duplicates and field blanks, shall have a completely filled-in sample tag securely attached to it. Duplicates and field blanks shall be so identified in the "Remarks" section of the tag.

After the collected samples have been transferred to the Sample Bank and documented there, they are renumbered and identified with a new sample analysis tag for shipment to analytical laboratories. This renumbering step enables the submittal of duplicate samples and QC samples as blinds to the analytical laboratory; analytical method blanks and calibration standards are identified as such. The same analysis tag (Figure 6-1) is used for all samples; it is a different color and numbered with a block of numbers different from other tags.

6.2.2 Sample Transfer Procedures/Chain-of-Custody Records

There are many transfers of custody in this program since materials are shipped to the Sample Bank for distribution to the sampling team or inclusion with collected samples, and shipped from the Sample Bank to analytical laboratories. The collection medium used for air sampling becomes part of the sample itself after collection; therefore, the laboratory preparing Tenax cartridges or polyurethane foam plugs must initiate a custody record and include it with their shipment of Tenax or foam. Laboratories providing QC samples must also initiate a custody record.

A. Chain-of-Custody Record Sheets

Customized record sheets, following the NEIC format, have been provided for this program; page 4 of this section shows the custody record used for all shipping of samples to analytical laboratories. Other similar forms are used to transfer custody of collection media, QC samples and collected samples. The custody record sheets are two-part carbonless copy forms which correlate with the sample identification tags; requested information has the same heading on both.

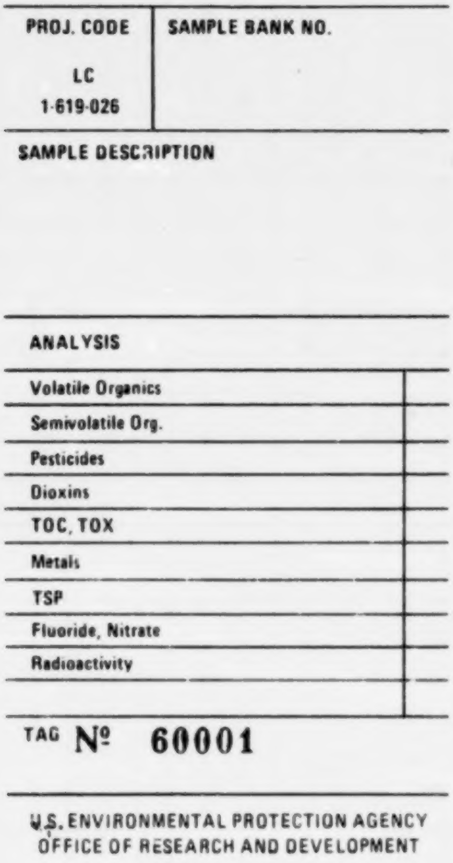
The custody records are used for a packaged lot of samples; more than one sample will usually be recorded on one form. More than one custody record sheet may be used for one package, if necessary. Their purpose is to document the transfer of a group of samples traveling together; when the group of samples changes, a new custody record is initiated. The original of the custody record always travels with the samples; the initiator of the record keeps the copy. When custody of the same group of samples changes hands several times, some people will not have a copy of the custody record. This is acceptable as long as the original custody record shows that each person who had received custody has properly relinquished it.

B. Using the Custody Record Sheet

- The originator fills in all requested information from the sample tags (except in the case of air collection media and external QC samples).

- The person receiving custody checks the sample tag information against the custody record. He also checks sample condition and notes anything unusual under "Remarks" on the custody form.

- The originator signs in the top left "Relinquished by" box and keeps the copy.



PROJ. CODE LC 1-619-026	**SAMPLE BANK NO.**

SAMPLE DESCRIPTION

ANALYSIS

Volatile Organics	
Semivolatile Org.	
Pesticides	
Dioxins	
TOC, TOX	
Metals	
TSP	
Fluoride, Nitrate	
Radioactivity	

TAG Nº 60001

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT

Figure 6-1. Analysis tag.

ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development

CHAIN OF CUSTODY RECORD

Project Code	Project Name
LC	LOVE CANAL STUDY (1-619-026)

TO:

	SAMPLE DESCRIPTION							ANALYSIS									
Sample Bank No.	Tenax	Polyfoam	Hi-Vol	Water	Soil	Sediment	Other	Volatile Organics	Semivolatile Organics	Pesticides	Dioxins	TOC, TOX	Metals	TSP	Fluoride, Nitrate	Radioactivity	REMARKS

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Relinquished by: (Signature)	Date/Time	Received for Laboratory by: (Signature)	Date/Time	Remarks	

№ 2000 Distribution: Original Accompanies Shipment; Copy to Sample Bank Files

- The person receiving custody signs in the adjacent "Received by" box and keeps the original.
- The Date/Time will be the same for both signatures since custody must be transferred to another person.
- When custody is transferred to the Sample Bank or an analytical laboratory, blank signature spaces may be left and the customized last "Received by" signature box used. Another approach is to run a line through the unused signature boxes.
- In all cases, it must be readily seen that the same person receiving custody has relinquished it to the next custodian.

C. Custody Record Used for Transfer to Analytical Laboratories (page 4)

- Initiated by Sample Bank.
- Custody transferred to shipper, such as Federal Express, before packing the original or custody form in with the samples.
- Shipper does not keep copy of custody form. Sample Bank keeps it with a copy of the bill of lading.
- Custody transferred to analytical lab which keeps original record.
- Analytical Lab Document Control Officer maintains original custody record until transmittal of complete project document inventory to GCA at completion of project activity.

D. Questions/Problems Concerning Custody Records

If a discrepancy between sample tag numbers and custody record listings is found, the person receiving custody should document this and properly store the samples. The samples should not be analyzed until the problem is resolved by contacting the GCA QA Manager or other designated responsible authority.

The responsible person receiving custody should attempt to resolve the problem by checking all available information (other markings on sample container, type of sample, etc.). He should then document the situation on the custody record and in his project logbook and notify the GCA QA Manager by the fastest available means, followed by written notification.

Changes may be written in the "Remarks" section of the Custody record and should be initialed and dated. A copy of this record should accompany the written notification to the QA Manager.

6.2.3 Custody Seals

Custody seals are narrow strips of adhesive paper used to demonstrate that no tampering has occurred. They may be used on sampling equipment or a house door, but they are intended for use on a sample transport container which is not secured by a padlock. They are not intended for use on individual sample containers.

6.2.4 Custody of Shipped Samples

When a group of samples with its custody form is to be shipped, the shipper (e.g., Federal Express) must sign the custody record before the package is closed so that he can verify the number and identification of the samples if he so desires. The shipper is not required to do so.

The package is then closed with a strong, keyed padlock or strapping tape and custody seals.

NEIC's recommended procedure for custody seal use on shipping boxes is as follows:

- Place paper side of seal against box and wrap strapping tape across the middle of the seal and at least twice around the box.
- Cut the tape so that the ends overlap at the seal.
- Fold the seal to itself over this overlap and sign the custody seal.
- Repeat this procedure as many times as necessary to seal the box for shipment.

The person receiving custody of shipped samples must document the condition of the locked, or strapped and sealed shipping box on arrival. It must be checked that neither the tape or the custody seals has been cut or otherwise tampered with. If the paper seal has been damaged in shipping but it is clear that the shipping box has not been opened, further handling of the samples may proceed. If tampering is suspected, the designated Sample Custodian shall notify the GCA Sample Bank.

6.2.5 Laboratory Custody Procedures

The Sample Bank, the sampling subcontractor's laboratory area, and each subcontracting analytical laboratory are considered to be working laboratories. Each laboratory shall have a designated Sample Custodian who implements a system to maintain control of samples. It is assumed that the laboratory is not open to the general public but has access restricted to employees known to each other. Each handling of the sample to renumber, subdivide, preserve, etc. does not have to be documented in this situation. Each subcontractor shall describe his laboratory custody procedures in his QA Plan. Special care should be given to internal cross-checks which identify extracts and aliquots.

of the same sample. Extracts which are sealed and stored for later transfer to GCA or EPA must remain under custody of the analytical laboratory until transfer. The laboratory's custody records form part of the overall project document inventory.

7.0 REFERENCE MATERIAL

The following pages contain standard reference materials applicable to analyses conducted as part of the Love Canal Study. Organization of these materials is as follows:

Section	Procedure	Page	Revision
7.1	METHOD 603 - ACROLEIN, ACRYLONITRILE	1 of 7	0
7.2	METHOD 605 - BENZIDINES	1 of 4	0
7.3	METHOD 608 - ORGANOCHLORINE PESTICIDES AND PCBs	1 of 10	0
7.4	METHOD 624 - PURGEABLES	1 of 9	0
7.5	METHOD 625 - BASE/NEUTRALS, ACIDS AND PESTICIDES	1 of 14	0
7.6	DIOXINS	1 of 1	0
7.7	QUALITATIVE ANALYSIS BY GC/MS	1 of 1	0
7.8	METALS BY ATOMIC ABSORPTION SPECTROMETRY	1 of 83	0

METHOD 603--ACROLEIN AND ACRYLONITRILE REPRODUCED FROM THE FEDERAL REGISTER/VOL. 44, NO. 233/ DECEMBER 3, 1979, PP. 69479-69484

Acrolein and Acrylonitrile—Method 603

1. *Scope and Application.*

1.1 This method covers the determination of acrolein and acrylonitrile. The following parameters may be determined by this method:

Parameter	*Storet No.*
Acrolein	34210
Acrylonitrile	32415

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 represent sensitivities that can be achieved in wastewaters under optimum operating conditions.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 An inert gas is bubbled through a 5 ml water sample contained in a specially-designed heated purging chamber. Acrolein and acrylonitrile are transferred from the aqueous phase to the vapor phase. The vapor is passed through a short sorbent tube where the compounds are trapped. After the extraction is completed, the trap is heated and backflushed with gas to desorb the compounds into a gas chromatographic system. A temperature program is used in the GC system to separate the compounds before detection with a flame ionization detector.

3. *Interferences.*

3.1 Impurities in the purge gas and organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) through the septum seal into the sample during shipment and storage. A sample blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce the likelihood of this, the purging device and sample syringe should be rinsed out twice between samples with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross-contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high organohalide levels it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105° C oven between analyses.

3.4 Interferences are sometimes reduced or eliminated by first purging the water samples for 5 minutes at room temperature in 9.4. Then the purge device is rapidly heated to 85° C and purged as in 9.4. With such a modification, approximately 5 to 10% of the acrylonitrile and a trace of the acrolein in the sample will be lost. Therefore, calibration must be established for the compounds under the conditions of this modified procedure.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete sampling.

4.1.1 Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105° C before use.

4.1.2 Septum-Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105° C for one hour before use.

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: the purging device, trap, and desorber. The purging device should be equipped for heating in the same manner as the trap (electrically) or with a circulating water jacket. If electrical heating is used the electrical parts must be protected so that water will not drip on the conductors, causing dangerous electrical shock or shorts. All temperature parameters must be carefully controlled. Several complete devices are available commercially although most are not equipped to heat the purging chamber. The device must meet the following specifications: the unit must be completely compatible with the gas chromatographic system; the purging chamber must be designed for a 5 ml volume and be modeled after Figure 1; the dimensions for the sorbant portion of the trap must meet or exceed those in figure 2. Figures 3 and 4 illustrate the complete system in the purge and the desorb mode.

4.3 Gas chromatograph—Analytical system complete with programmable gas chromatograph suitable for on-column injection, equipped with matched columns for dual column analysis and a differential flame ionization detector. A nitrogen specific detector (thermionic or Hall) may be used if only acrylonitrile is to be detected. Required accessories include: column supplies, recorder, and gases. A data system for measuring peak areas is recommended.

4.4 Syringes—5-ml glass hypodermic with luerlok tip (2 each).

4.5 Micro syringes—10, 25, 100 ul.

4.6 2-way syringe valve with Luer ends (3 each).

4.7 Bottle—15-ml screw-cap, with Teflon cap liner.

5. *Reagents.*

5.1 Preservatives

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2. Sulfuric acid—(ACS). Mix equal volumes of conc. H_2SO_4 with distilled water.

5.1.3 Sodium thiosulfate—(ACS) Granular.

5.2 Trap absorbent—Porous polymer packing, 50/80 mesh chromatographic grade Porapak N.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water.

5.4.1 Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon.

5.4.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

5.4.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle and seal with a Teflon lined septum and cap.

5.5 Stock standards—Prepare stock standard solutions daily in water using assayed standards. Because of toxicity, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of the materials.

5.5.1 Place about 9.8 ml of water (pH 6.5 to 7.5) into a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all water wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Using a 100 ul syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the water without contacting the neck of the flask.

5.5.3 Dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15 ml screw-cap bottle with a Teflon cap liner.

5.5.4 Calculate the concentration in micrograms per microliter from the net gain in weight.

6. *Calibration.*

6.1 Using stock standards, prepare secondary dilution standards in water. The standards should be prepared at concentrations such that the aqueous standards prepared in 6.2 will completely bracket the working range of the chromatographic system.

6.2 Using secondary dilution standards, prepare calibration standards by carefully adding 20 ul of stock standard to 100, 500, or 1000 ml of organic-free water.

6.3 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting secondary dilution standards, establish the sensitivity limit and the linear range of the analytical system for each compound.

6.4 Assemble the necessary purge and trap device. The trap must meet the minimum specifications as shown in Figure 2 to achieve satisfactory results. Condition the trap overnight at 180° C by backflushing with an inert gas flow of at least 20 ml/min. Prior to use, daily condition traps 10 minutes while backflushing at 180° C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 9. Compare the responses to those obtained by injection of standards (6.3), to determine purging efficiency and also to calculate analytical precision. The purging efficiencies and analytical precision of the analysis of aqueous standards should be 85±5% for acrolein and 98±5% for acrylonitrile.

6.5 By analyzing calibration standards, establish the sensitivity limit and linear range of the entire analytical system for each compound.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water method blank that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and blank with surrogate compounds.

8. *Sample Collection, Preservation, and Handling.*

8.1 Collect about 500 ml sample in a clean container. Adjust the pH of the sample to 6.5 to 7.5 by adding 1:1 diluted H_2SO_4 or NaOH while stirring vigorously. If the sample contains residual chlorine, add 35 mg of sodium thiosulfate per part per million of free chlorine per liter of sample. Fill a 40 ml sample bottle and seal the bottle so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

8.2 The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

8.3 All samples must be analyzed within 3 days of collection.

9. *Sample Extraction and Gas Chromatography.*

9.1 Adjust the helium purge gas flow rate to 20±1 ml/min and the temperature of the purge device to 85°C. Attach the trap inlet to the purging device, and set the device to purge. Open the syringe valve located on the purging device sample introduction needle.

9.2 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the water into the syringe barrel until it oveflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml.

9.3 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.4 Close both valves and purge the sample for 30.0±0.1 minutes. Monitor and control the temperature of the purge device to obtain 85±1°C.

9.5 After the 30-minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly hearing the trap to 170°C while backflushing the trap with helium at 45 ml/min for 5 minutes. The backflushing time and gas flow rate must be carefully reproduced from sample to sample. During blackflushing the chromatographic column is held at 100°C. Record GC retention time from the beginning of desorption.

9.6 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5 ml flushes of organic-free water.

9.7 After desorbing the sample for 5 minutes recondition the trap by returning the purge and trap device to the purge mode and begin the GC progrm. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 170°C. After approximately seven minutes turn off the trap heater and open the syringe valve to stop the gas flow through the trap. when cool the trap is ready for the next sample.

9.8 Table 1 summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by this column is shown in Figure 5. Calibrate the system daily by analysis of a minimum of three concentrations levels of calibration standards.

10. *Calculations.*

10.1 Determine the concentration of individual compounds directly from calibrations plots of concentration (ug/l) vs. peak height or area units.

10.2 Report results in micrograms per liter. When duplicate and spiked samples are analyzed, all data obtained should be reported.

11. *Accuracy and precision*

The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

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3. "Development and application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 11–Purgeables and Category 12–Acrolein, Acrylonitrile, and Dichlorodifluoromethane." Report for EPA Contract 68–03–2635 (In preparation).

4. Going, John, et al., "Environmental Monitoring Near Industrial Sites-Acrylonitrile," EPA Report No. 560/6–79–003, 1979.

Table 1.—*Gas Chromatography by Heated Purge and Trap*

Compound [1]	Retention Time (min.)	Detection Limit ug/1 [2]
Acrolein	7.6	2
Acrylonitrile	8.8	

[1] Column conditions: Chromosorb 101 80/100 mesh packed in a 6' × ⅛" O.D. stainless steel column with helium carrier gas at 45 m1/min flow rate. Column temperature is held at 100° C for 5 minutes during trap desorption, then programmed at 10 ° C/min to 140 °C and held for 5 minutes.

[2] Detection limit is estimated, based upon the use of a flame ionization detector.

BILLING CODE 6560-01-M

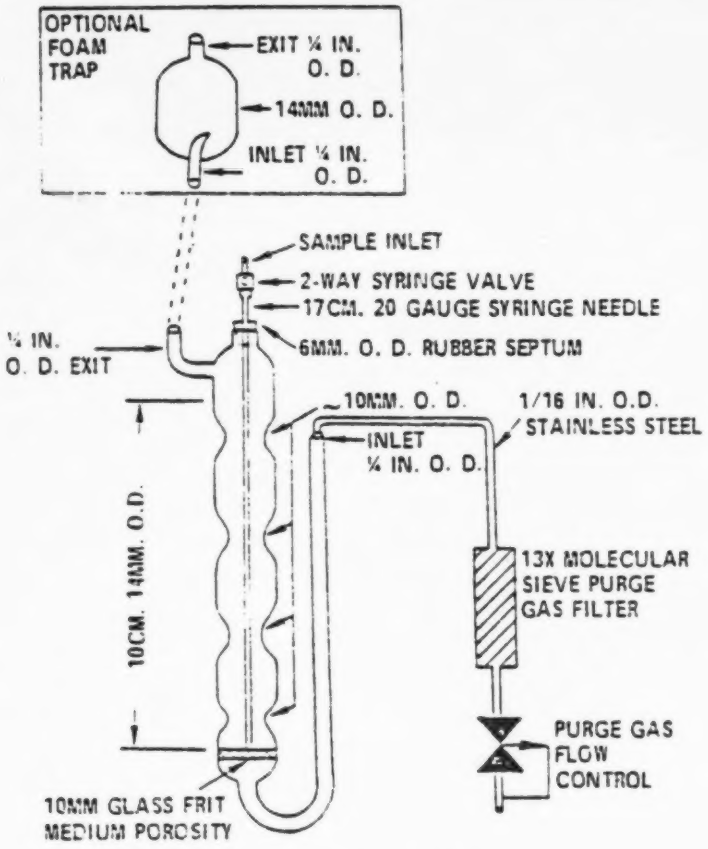
OPTIONAL FOAM TRAP
EXIT ¼ IN. O. D.
14MM O. D.
INLET ¼ IN. O. D.
SAMPLE INLET
2-WAY SYRINGE VALVE
17CM. 20 GAUGE SYRINGE NEEDLE
¼ IN. O. D. EXIT
6MM. O. D. RUBBER SEPTUM
10MM. O. D
1/16 IN. O.D. STAINLESS STEEL
INLET ¼ IN. O. D.
10CM. 14MM. O.D.
13X MOLECULAR SIEVE PURGE GAS FILTER
PURGE GAS FLOW CONTROL
10MM GLASS FRIT MEDIUM POROSITY

Figure 1. Purging device

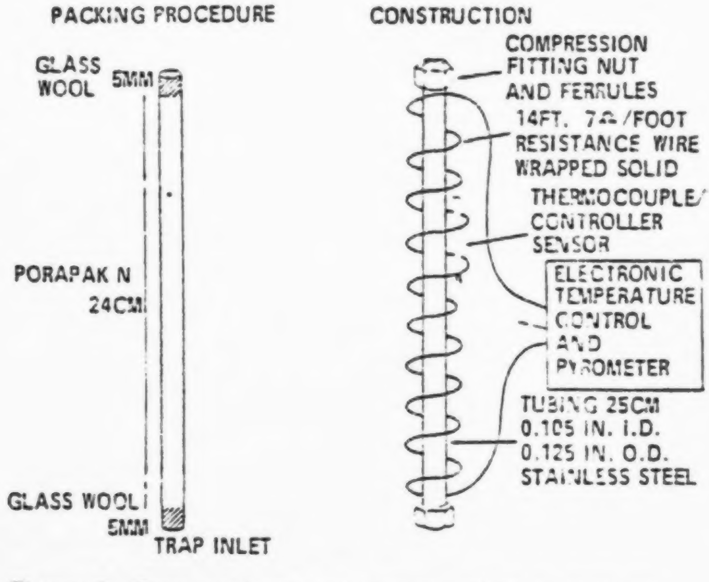
PACKING PROCEDURE
CONSTRUCTION
GLASS WOOL 5MM
PORAPAK N 24CM
GLASS WOOL 5MM
TRAP INLET
COMPRESSION FITTING NUT AND FERRULES
14FT. 7Ω/FOOT RESISTANCE WIRE WRAPPED SOLID
THERMOCOUPLE/ CONTROLLER SENSOR
ELECTRONIC TEMPERATURE CONTROL AND PYROMETER
TUBING 25CM 0.105 IN. I.D. 0.125 IN. O.D. STAINLESS STEEL

Figure 2. Trap packings and construction to include desorb capability

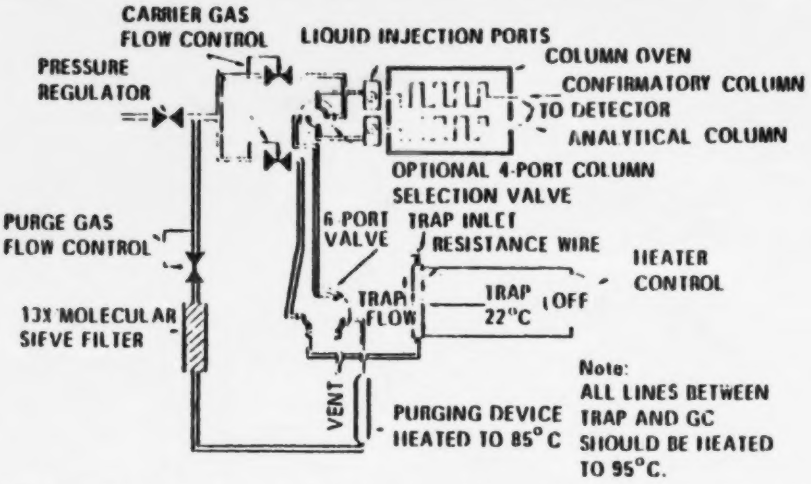
CARRIER GAS
FLOW CONTROL
LIQUID INJECTION PORTS
PRESSURE
REGULATOR
COLUMN OVEN
CONFIRMATORY COLUMN
TO DETECTOR
ANALYTICAL COLUMN
OPTIONAL 4-PORT COLUMN
SELECTION VALVE
PURGE GAS
FLOW CONTROL
6 PORT
VALVE
TRAP INLET
RESISTANCE WIRE
HEATER
CONTROL
TRAP
FLOW
TRAP
22°C
OFF
13X MOLECULAR
SIEVE FILTER
VENT
PURGING DEVICE
HEATED TO 85°C
Note:
ALL LINES BETWEEN
TRAP AND GC
SHOULD BE HEATED
TO 95°C.

Figure 3. Schematic of purge and trap device - purge mode

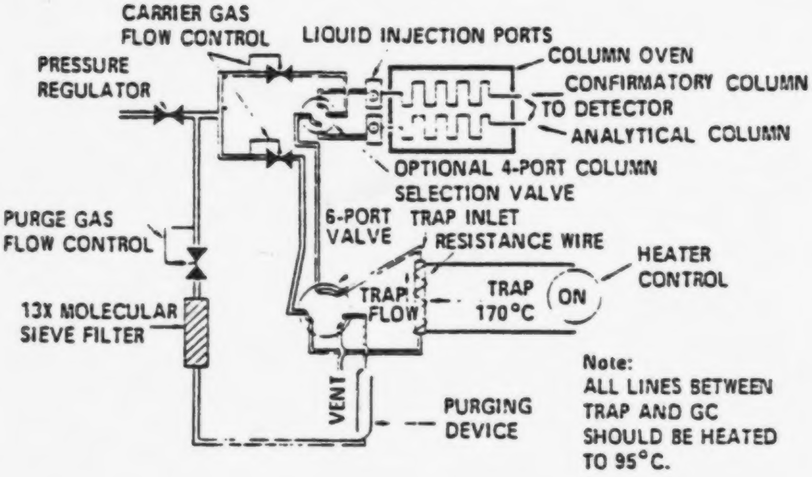
CARRIER GAS
FLOW CONTROL
LIQUID INJECTION PORTS
PRESSURE
REGULATOR
COLUMN OVEN
CONFIRMATORY COLUMN
TO DETECTOR
ANALYTICAL COLUMN
OPTIONAL 4-PORT COLUMN
SELECTION VALVE
PURGE GAS
FLOW CONTROL
6-PORT
VALVE
TRAP INLET
RESISTANCE WIRE
HEATER
CONTROL
TRAP
FLOW
TRAP
170°C
ON
13X MOLECULAR
SIEVE FILTER
VENT
PURGING
DEVICE
Note:
ALL LINES BETWEEN
TRAP AND GC
SHOULD BE HEATED
TO 95°C.

Figure 4. Schematic of purge and trap device - desorb mode

BILLING CODE 6560-01-C

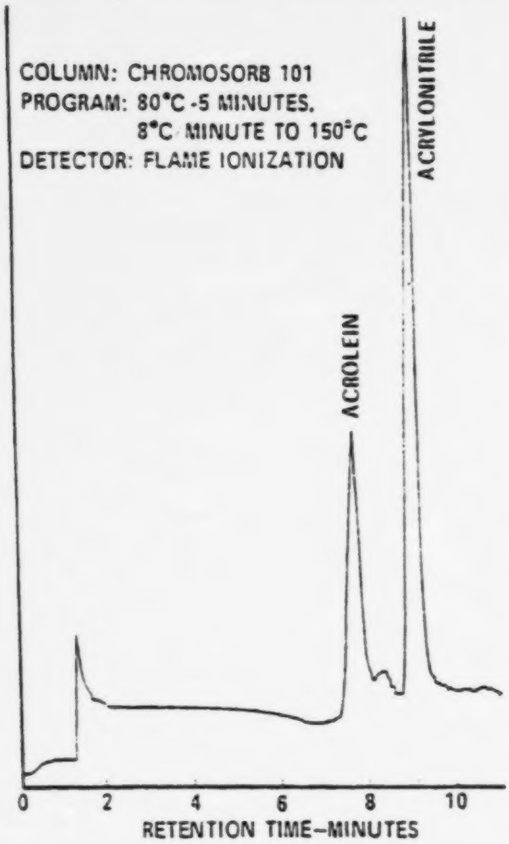

Figure 5. Gas chromatogram of acrolein and acrylonitrile

Phenols—Method 604

1. *Scope and Application.*

1.1 This method covers the determination of various phenolic compounds. The following parameters may be determined by this method:

Parameter	*Storet No.*
4-Chloro-3-methylphenol	34452
2-Chlorophenol	34586
2,4-Dichlorophenol	34601
2,4-Dimethylphenol	34606
2,4-Dinitrophenol	34616
2-Methyl-4,6-dinitrophenol	34657
2-Nitrophenol	34591
4-Nitrophenol	34646
Pentachlorophenol	39032
Phenol	34694
2,4,6-Trichlorophenol	34621

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters with a flame ionization detector in the absence of interferences. If the derivatization cleanup is required, the sensitivity of the method is 10 $\mu g/1$. This concentration represents the minimum amount proven to date to give reproducible and linear response during derivatization.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is acidified and extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Flame ionization gas chromatographic conditions are described which allow for the measurement of the compounds in the extract.

2.2 The method also provides for the preparation of pentafluorobenzylbromide (PFB) derivatives for electron capture gas chromatography with additional cleanup procedures to aid the analyst in the elimination of interferences.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

METHOD 605--BENZIDINES REPRODUCED FROM THE FEDERAL REGISTER/VOL. 44, NO. 233/ DECEMBER 3, 1979, PP. 69489-69491

Benzidines—Method 605

1. *Scope and Application.*

1.1 This method covers the determination of benzidine and selected derivatives. The following parameters may be determined by this method:

Parameter	*Storet No.*
Benzidine	39120
3,3'-Dichlorobenzidine	34631

1.2 This method is applicable to the measurement of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identifications implied with the use of these techniques.

1.3 This sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 Benzidine and 3,3-dichlorobenzidine (DCB) are extracted from the sample at pH 7–8 using chloroform. The extract is then back extracted into acid, re-extracted into chloroform at neutral pH, and concentrated. The benzidines are determined in the final extract using high performance liquid chromatography (HPLC) with electrochemical detection.

2.2 If interferences are encountered with the measurement of benzidine, the method provides additional detector settings to increase the selectivity of the analytical system.

3. *Interferences.*

3.1 Although the detection system is highly selective, solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

3.3 Some dye plant effluents contain large amounts of components with retention times in the vicinity of benzidine. In these cases, it has been found useful to reduce the electrode potential in order to eliminate the interferences but still detect the benzidine.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-pint or 1-quart volume. Quart bottles should be only half filled in the field. French or Boston Round design is recommended. The container should be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if the sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing or fittings may be used in the system.

4.2 Separatory funnel—1000 ml and 250 ml, with Teflon stopcock.

4.3 Water bath—Heated, with concentric ring cover, capable of temperature control within 2°C. The bath should be used in a hood.

4.4 Rotating evaporator.

4.5 Flasks—round bottom, 100 ml, with 24/40 joints.

4.6 Centrifuge tubes—conical, screw capped, graduated, with Teflon lined caps.

4.7 Pipettes—Pasteur, with bulbs.

4.8 High performance liquid chromatograph—Analytical system complete with column supplies, recorder, syringes, and the following components:

4.8.1 Solvent delivery system—with pulse damper (Altex 110A, or equivalent).

4.8.2 Injection valve Waters Model USK (or equivalent).

4.8.3 Electrochemical detector Bioanalytical Systems LC-2A with glassy carbon electrode, (or equivalent).

4.8.4 Electrode polishing kit Princeton Applied Research Model 9320 (or equivalent).

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid—(ACS) Mix equal volumes in conc. H_2SO_4 with distilled water.

5.1.3 Sodium thiosulfate—(ACS) granular.

5.2 Sulfuric acid (1M)—(ACS) 58 ml/liter in distilled water.

5.3 Sodium hydroxide (20%)—(ACS) 20 grams/100 ml in distilled water.

5.4 Sodium hydroxide (IM)—(ACS) 40 grams/liter in distilled water.

5.5 Sodium tribasic phosphate (0.4M)—(ACS) 160 grams Na_3PO_4 $(12H_2O)$ in 1 liter of distilled water.

5.6 Acetate buffer 0.1*M*, pH 4.7; 5.8 mls glacial acetic acid (ACS) and 13.6 grams of sodium acetate trihydrate (ACS) per liter in distilled water.

5.7 Acetonitrile—Pesticide quality or equivalent.

5.8 Methyl alcohol—Pesticide quality or equivalent.

5.9 Chloroform (preserved with 1% ETOH)—Burdick and Jackson (or equivalent).

5.10 Water—Purified (e.g. from Millipore RO–4 System or equivalent).

5.11 HPLC mobile phase—Place 1 liter of filtered (through Millipore type FH filter, or equivalent) acetonitrile and 1 liter of filtered (through Millipore type GS filter, or equivalent) acetate buffer in a narrow mouth, glass, one gallon jug and mix thoroughly. Prepare fresh weekly.

5.12 Stock standards—Prepare stock standard solutions at a concentration of 0.100 ug/μl by dissolving 0.0100 gram of assayed reference material in pesticide quality methyl alcohol and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared from the stock standards at the following concentrations that will bracket the working range of the chromatographic system:

Solution Conc. (ng/μl)	Sensitivity (nA Full Scale)
0.05	10
0.10	10
0.50	50
1.0	100
5.0	500

6.2 Assemble the necessary liquid chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I.

6.3 A constant injection volume of 25 microliters should be employed for all subsequent measurements.

6.4 In order to determine the precision of the HPLC system, a series of 6 replicate injections of a 1 ng/μl solution of benzidine and 3,3'-dichlorobenzidine (DCB) should be made on the 50nA full scale setting. A precision of ±4% should be achieved for the peak heights of both benzidine and DCB. This measurement should be made every few weeks or whenever instrument related problems are apparent. A sample chromatogram is shown in Figure 1.

6.5 Retention times should remain relatively constant (within ±5% day to day) with benzidine being 6.1 minutes and DCB being 12.1 minutes under the specified conditions. These values should be checked daily when the calibration injections are made.

6.6 If serious loss of response occurs, it may be necessary to polish the surface of the carbon electrode (according to the instructions supplied with the polishing kit). In this case, it will be necessary to recalibrate the system.

6.7 When leaving the instrument idle, it is advisable to maintain a flow of 0.1 ml/min of mobile phase through the HPLC column in order to prolong column life.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection to extraction. Benzidine and dichlorobenzidine are easily oxidized by materials such as free chlorine. For chlorinated wastes, *immediately* add 35 mg sodium thiosulfate per part per million of free chlorine per liter.

8.3 If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4 ±0.2 units to prevent rearrangement to benzidine. Otherwise, if the samples will not be extracted within 48 hours of collection, the sample pH should be adjusted to 2–3 with sodium hydroxide or sulfuric acid.

8.4 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Quantitatively pour the entire sample into a one-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 6.5–7.5 with sodium hydroxide or sulfuric acid.

9.2 Add 100 ml chloroform to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes. Allow the organic layer to separate from the sample a minimum of ten minutes, then collect the chloroform extract in a 250-ml separatory funnel.

9.3 Add 50 ml chloroform to the sample bottle and complete the extraction procedure a second time, combining the extracts in the separatory funnel. Perform a third extraction in the same manner with an additional 50 ml volume.

9.4 Discard any aqueous layer from the 250 ml funnel containing the combined organic layers. Add 25 ml of l M sulfuric acid and extract the sample by shaking the funnel for two minutes. Transfer the aqueous layer to a 250 ml beaker. Extract with two additional 25 ml portions of l M sulfuric acid and combine the acid extracts in the beaker.

9.5 Place a stirbar in the 250 ml beaker and stir the acid extract while carefully adding 5 ml of a .4M sodium tribasic phosphate. With the aid of a pH meter neutralize the extract to pH 6–7 by dropwise addition of 20 percent NaOH while stirring the solution vigorously. Approximately 25–30 ml of 20 percent NaOH will be required and it should be added over at least a 2-minute period. Do not allow the sample pH ever to exceed pH 8.

9.6 Pour the neutralized extract into a 250 ml separatory funnel. Add 30 ml of chloroform and shake the funnel for 2 minutes. Allow phases to separate, and transfer the organic layer in a second 250 ml separatory funnel.

9.7 Extract the aqueous layer with two additional 20 ml aliquots of chloroform as before. Combine the extracts in the 250 ml separatory funnel.

9.8 Add 20 ml of distilled water to the combined organic layers, shake for 30 seconds, and discard aqueous layer.

9.9 Transfer the organic extract into a 100 ml round bottom flask. Add 20 ml of methyl alcohol and concentrate to 5 ml on a rotating evaporator at 35°C.

9.10 Using a 9-inch Pasteur pipette, transfer the extract to a 15 ml conical scew-capped centrifuge tube. Rinse the flask, including the entire side wall, with two ml portions of methyl alcohol and combine with the original extract.

9.11 Carefully concentrate the extract to 0.5 ml using a gentle stream of nitrogen and a 30°C water bath, dilute to 2 ml with methyl alcohol, reconcentrate to 1 ml, and dilute to 5 ml with acetate buffer. Mix extract thoroughly. Stopper the ampul and store refrigerated if further processing with not be performed immediately.

9.12 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. Liquid Chromatography (HPLC).

10.1 Table I summarizes the recommended liquid chromatographic column material and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by this column is shown in Figure 1. Calibrate the system daily with a minimum of three injections of calibration standards.

10.2 Inject 25 ul of the sample extract. If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

10.3 If the peak area measurement for benzidine is prevented by the presence of interferences, reduce the electrode potential to 0.7 V and reanalyze.

11. Calculations.

11.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per unit peak area.

B = Peak size in injection of sample extract, in peak area units

V_i = Volume of extract injected(µl)

V_t = Volume of total extract (µl)

V_s = Volume of water extracted (ml)

11.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

12. Accuracy and Precision.

12.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters Category 7--Benzidines," Report for EPA Contract 68-03-2624 (In preparation).

Table I.—*Liquid Chromatography of Benzidines*

Compound [1]	Retention time (min.)	Detection limit (µg/l) [2]
Benzidine	6.1	0.05
3,3'-dichlorobenzidine	12.1	0.1

[1] Column conditions: Lichrosorb RP-2, 5 micron particle diameter, packed in a 25 cm × 4.6 mm ID stainless steel column with 0.8 ml/min flow rate of mobile phase (50 percent acetonitrile: 50 percent 0.1 M pH 4.7 acetate buffer).

[2] Detection limit is calculated from the minimum detectable response of the electrochemical detector at 0.8 volts being equal to five times the background noise, assuming a 5 ml final extract volume of the 500 ml sample, and assuming an injection volume of 25 microliters.

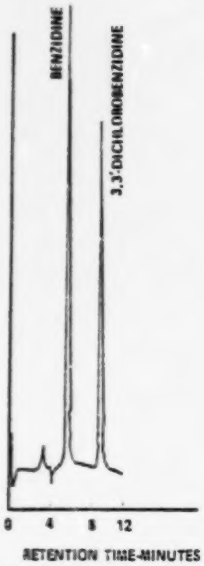

Figure 1. Liquid chromatogram of benzidines

Phthalate Esters—Method 606

1. *Scope and Application.*

1.1 This method covers the determination of certain phthalate esters. The following parameters may be determined by this method:

Parameter	Storet No.
Benzyl butyl phthalate	34292
Bis(2-ethylhexyl) phthalate	39100
Di-n-butyl phthalate	34110
Di-n-octyl phthalate	34596
Diethyl phthalate	34336
Dimethyl phthalate	34341

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the sample will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

3.3 Phthalate esters contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no phthalate residues contaminate the sample or solvent extract under the conditions of the analysis. Of particular importance is the avoidance of plastics because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

METHOD 608--ORGANOCHLORINE PESTICIDES AND PCBs; REPRODUCED FROM THE FEDERAL REGISTER, VOL. 44, No. 233, DECEMBER 3, 1979, PP. 69501-69509

Organochlorine Pesticides and PCB's—Method 608

1. *Scope and Application.*

1.1 This method covers the determination of certain organochlorine pesticides and polychlorinated biphenyls (PCBs). The following parameters may be determined by this method:

Parameter:	Storet No.
Aldrin	39330
a-BHC	39337
b-BHC	39338
d-BHC	39259
g-BHC	39340
Chlordane	39350
4,4'-DDD	39310
4,4'-DDE	39320
4,4'-DDT	39300
Dieldrin	39380
Endosuflan I	34361
Endosuflan II	34356
Endosuflan Sulfate	34351
Endrin	39390
Endrin Aldehyde	34366
Heptachlor	39410
Heptachlor Epoxide	39420
Toxaphene	39400
PCB-1016	34671
PCB-1221	39488
PCB-1232	39492
PCB-1242	39496
PCB-1248	39500
PCB-1254	39504
PCB-1260	39508

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table 1.

3.3 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing in hot water. Rinse with tap water, distilled water, acetone and finally pesticide quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400°C for 15 to 30 minutes. Some high boiling materials, such as PCBs, may not be eliminated by this treatment. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed/stored in a clean environment immediately after drying or cooling to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.4 Interferences by phthalate esters can pose a major problem in pesticide analysis. These materials elute in the 15% and 50% fractions of the Florisil cleanup. They usually can be minimized by avoiding contact with any plastic materials. The contamination from phthalate esters can be completely eliminated with the use of a microcoulometric or electrolytic conductivity detector.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at 1.0 and 10.0 ml level. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Boiling chips—extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required acessories including electron capture or halogen-specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic column—Pyrex, 400 mm × 25 mm OD, with coarse fritted plate and Teflon stopcock (Kontes K-42054-213 or equivalent).

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid (1+1)—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride—Pesticide quality or equivalent.

5.3 Sodium Sulfate—(ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 $\mu g/\mu l$ by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Boiling chips—Hengar granules (Hengar Co.; Fisher Co.) or equivalent.

5.6 Mercury—triple distilled.

5.7 Aluminum oxide—basic or neutral, active.

5.8 Hexane—pesticide residue analysis grade.

5.9 Isooctane (2,2,4-trimethyl pentane)—pesticide residue analysis grade.

5.10 Acetone—pesticide residue analysis grade.

5.11 Diethyl ether—Nanograde, redistilled in glass if necessary.

5.11.1 Must be free of peroxides as indicated by EM Quant test strips (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y., 10523).

5.1.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.12 Florisil—PR grade (60/100 mesh); purchase activated at 1250°F and store in glass containers with glass stoppers or foil-lined screw caps. Before use activate each batch at least 16 hours at 130°C in a foil covered glass container.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/l in the final extract, for example, prepare standards at 10 μg/l, 50 μg/l, 100 μg/l, 500 μg/l, etc., so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 The cleanup procedure in Section 10 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorption capacity. To standardize the amount of Florisil which is used, the use of lauric acid value (Mills, 1968) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 grams.

6.4 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must enploy mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K-D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K-D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.

9.6 Increase the temperature of the hot water bath to about 80°C. Momentarily remove the Snyder column, add 50 ml of hexane and a new boiling chip and reattach the Snyder column. Pour about 1 ml of hexane into the top of the Snyder column and concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml of hexane, and adjust the volume to 10 ml. A 5-ml syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis. If the sample requires cleanup, proceed to Section 10.

9.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. *Cleanup and Separction.*

10.1 Cleanup procedures are used to extend the sensitivity of a method by minimizing or eliminating interferences that mask or otherwise disfigure the gas chromatographic response to the pesticides and PCB's. The Florisil column allows for a select fractionation of the compounds and will eliminate polar materials. Elemental sulfur interferes with the electron capture gas chromatography of certain pesticides but can be removed by the techniques described below.

10.2 Florisil Column Cleanup

10.2.1 Add a weight of Florisil, (nominally 21g,) predetermined by calibration (6.3, 6.4), to a chromatographic column. Settle the Florisil by tapping the column. Add sodium sulfate to the top of the Florisil to form a layer 1–2 cm deep. Add 60 ml of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatography column. Discard the eluate.

10.2.2 Adjust the sample extract volume to 10 ml and transfer it from the K–D concentrator tube to the Florisil column. Rinse the tube twice with 1–2 ml hexane, adding each rinse to the column.

10.2.3 Place a 500 ml K–D flask and clean concentrator tube under the chromatography column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 ml of 6% ethyl ether in hexane (Fraction 1) using a drip rate of about 5 ml/min. Remove the K–D flask and set aside for later concentration. Elute the column again, using 200 ml of 15% ethyl ether in nexane (Fraction 2), into a second K–D flask. Perform the third elution using 200 ml of 50% ethyl in hexane (Fraction 3). The elution patterns for the pesticides and PCB's are shown in Table II.

10.2.4 Concentrate the eluates by standard K–D techniques (9.5), substituting hexane for the glassware rinses and using the water bath at about 85° C. Adjust final volume to 10 ml with hexane. Analyze by gas chromatography.

10.3 Elemental sulfur will usually elute entirely in Fraction 1. To remove sulfur interference from this fraction or the original extract, pipet 1.00 ml of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add 1–3 drops of mercury and seal. Agitate the contents of the vial for 15–30 seconds. Place the vial in an upright position on a reciprocal laboratory shaker and shake for 2 hours. Analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by these columns are shown in Figures 1 through 10. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 µl of the sample extract using the solvent-flush technique. Smaller (1.0 µl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µl, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (µl)

V_t = Volume of total extract (µl)

V_s = Volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.*

13.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 10–Pesticides and PCB's." Report for EPA Contract 68–03–2606.
2. Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, *51*, 29 (1968).

Table I. —*Gas Chromatography of Pesticides and PCB's*

Parameter	Retention time (min) Col. 1 [1]	Col.2 [2]	Detection limit (µg/1) [3]
Aldrin	2.40	4.10	0.003
a-BHC	1.35	1.82	0.002
b-BHC	1.90	1.97	0.004
d-BHC	2.15	2.20	0.004
g-BHC	1.70	2.13	0.002
Chlordane	(4)	(4)	0.04
4,4†-DDD	7.83	9.08	0.012
4,4†-DDE	5.13	7.15	0.006
4,4†-DDT	9.40	11.75	0.016
Dieldrin	5.45	7.23	0.006
Endosulfan I	4.50	6.20	0.005
Endosulfan II	8.00	8.28	0.01
Endosulfan sulfate	14.22	10.70	0.03
Endrin	6.55	8.10	0.009
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.002
Heptachlor epoxide	3.50	5.00	0.004
Toxaphene	(4)	(4)	0.40
PCB-1016	(4)	(4)	0.04
PCB-1221	(4)	(4)	0.10
PCB-1232	(4)	(4)	0.10
PCB-1242	(4)	(4)	0.05
PCB-1248	(4)	(4)	0.08
PCB-1254	(4)	(4)	0.08
PCB-1260	(4)	(4)	0.15

[1] Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180 cm long x 4 mm ID glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200°C.

[2] Supelcoport 100/120 mesh coated with 3% OV-1 in a 180 cm long x 4 mm ID glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200°C.

[3] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

[4] Multiple peak response. See Figures 2–10.

Table II. —*Distribution and Recovery of Chlorinated Pesticides and PCBs Using Florisil Column Chromatography*

Parameter	Recovery (percent) by fraction [1]		
	1(6 pct.)	2 (15 pct.)	3 (50 pct.)
Aldrin	100		
a-BHC	100		
b-BHC	97		
d-BHC	98		
g-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4c4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

[1] From: "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 10-Pesticides and PCB's. Report for EPA Contract 68-03-2606."

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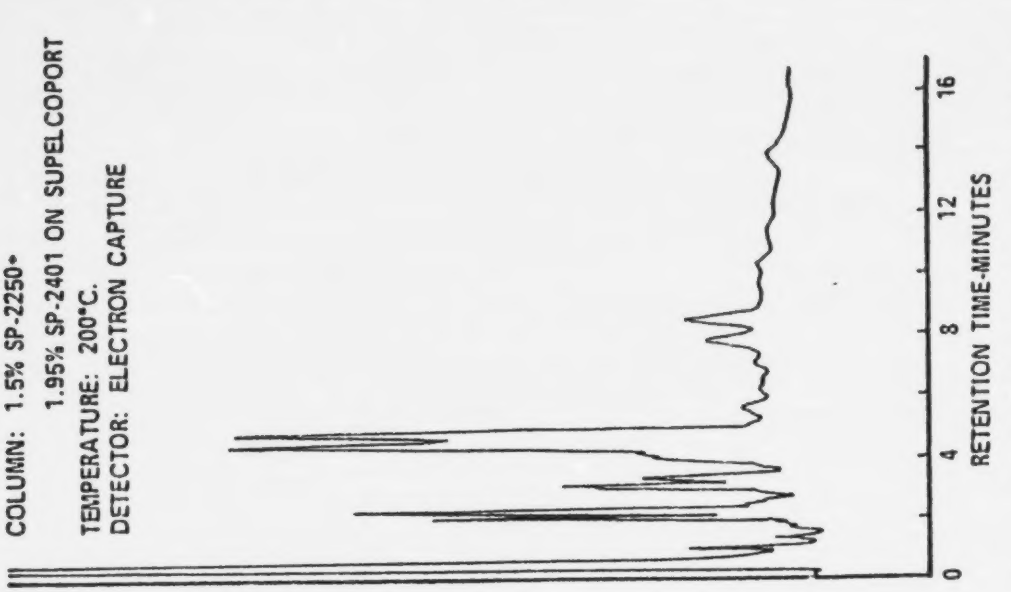

Figure 2. Gas chromatogram of chlordane

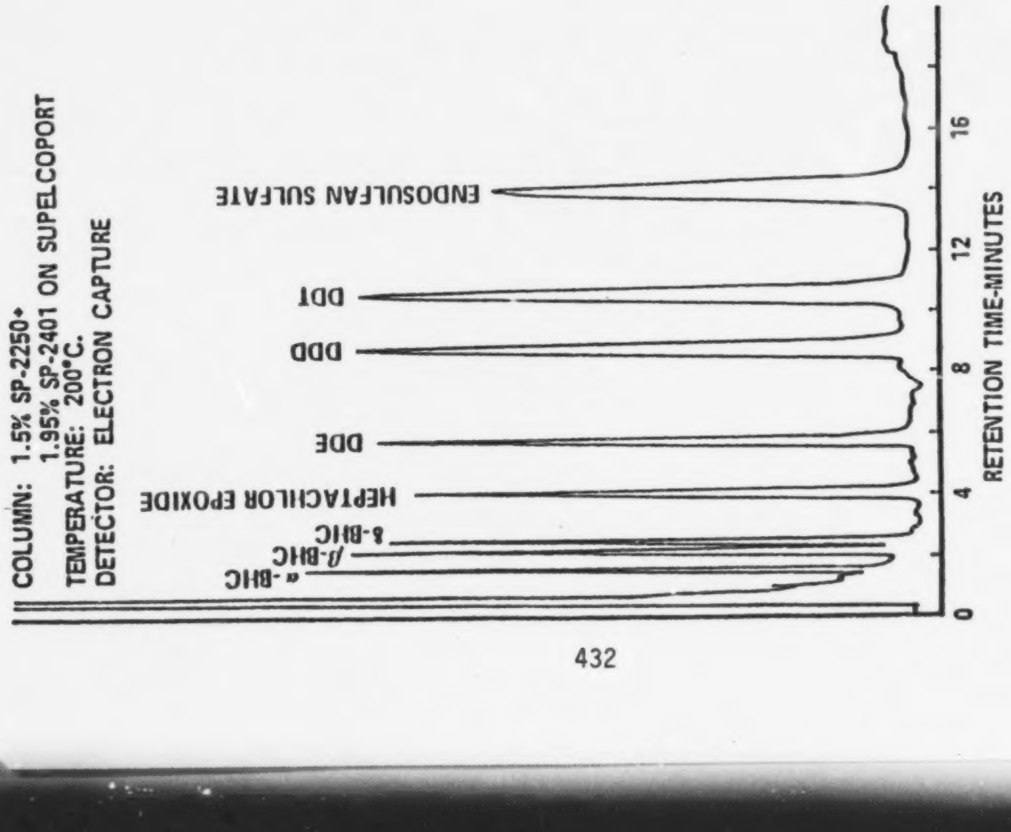

Figure 1. Gas chromatogram of pesticides

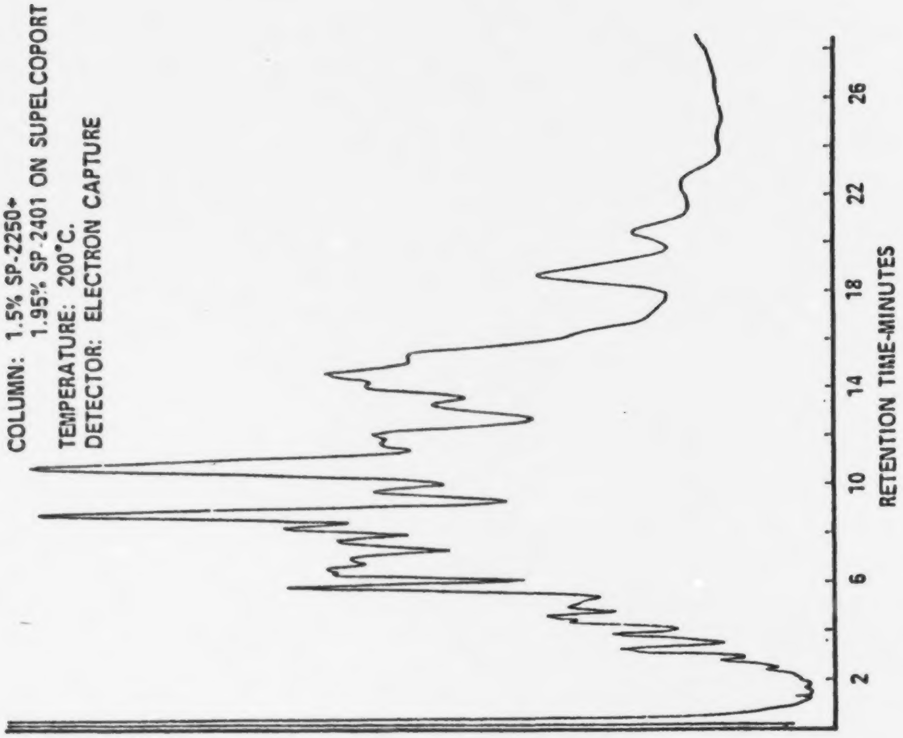

Figure 3. Gas chromatogram of toxaphene

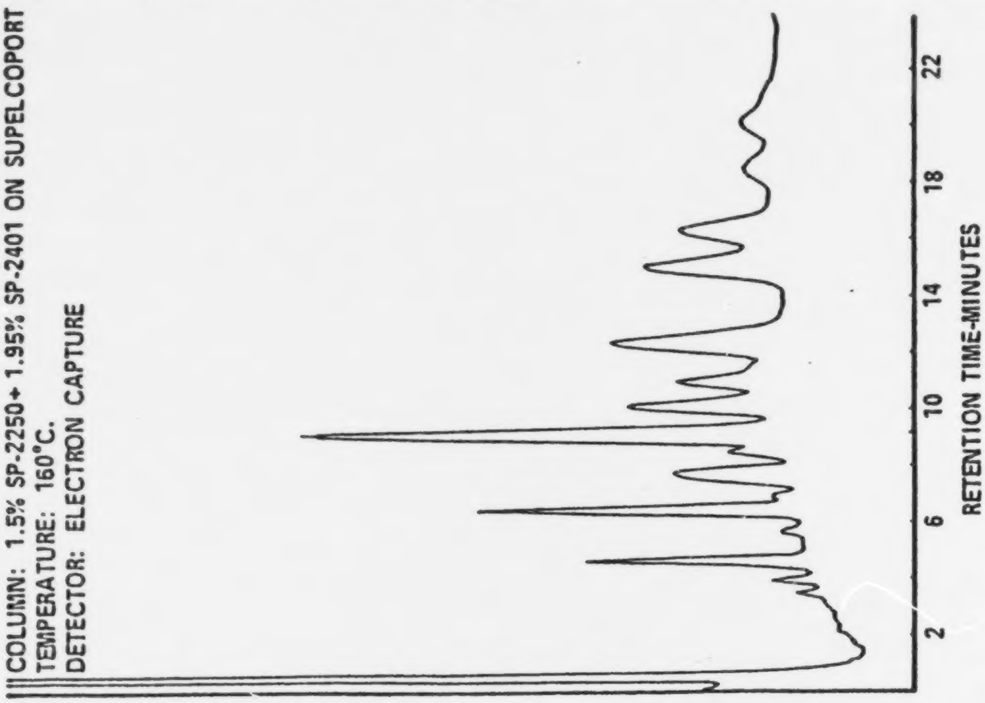

Figure 4. Gas chromatogram of PCB-1016

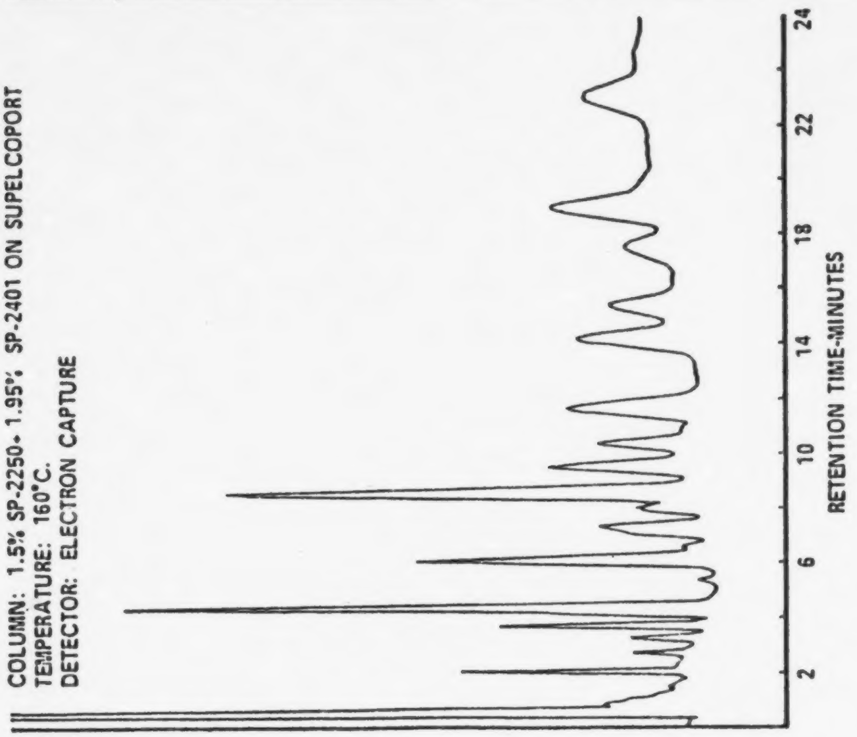

Figure 6. Gas chromatogram of PCB-1232

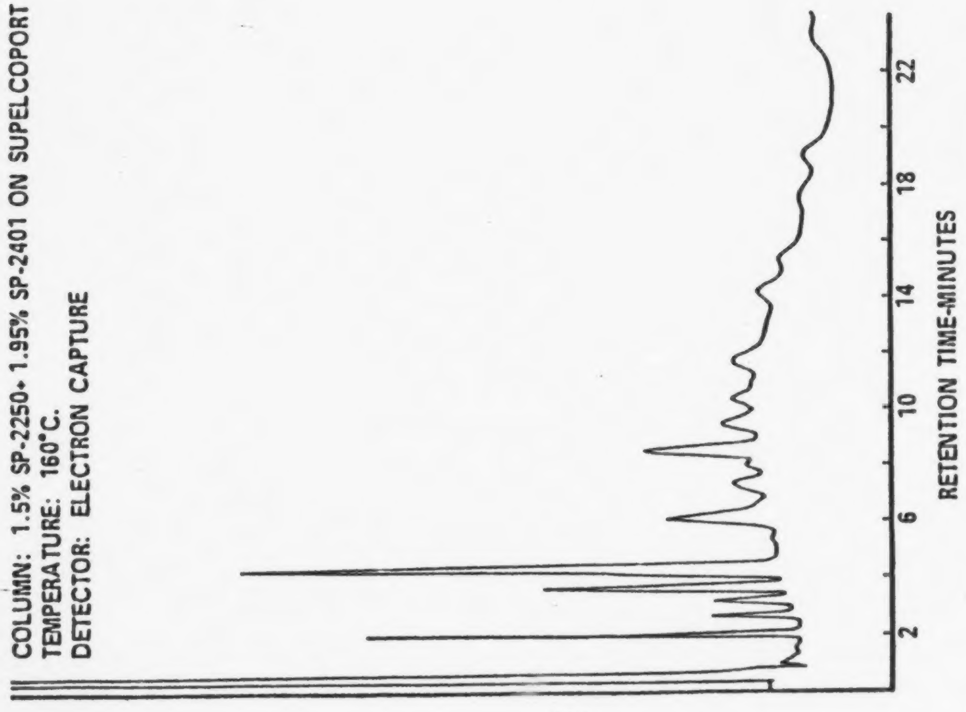

Figure 5. Gas chromatogram of PCB-1221

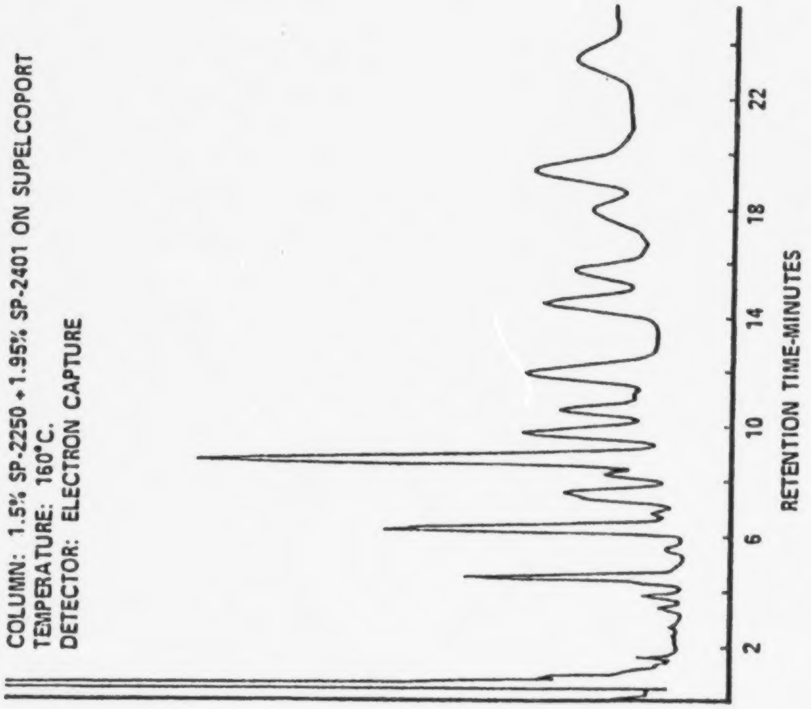
COLUMN: 1.5% SP-2250 + 1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 160°C.
DETECTOR: ELECTRON CAPTURE

Figure 7. Gas chromatogram of PCB-1242

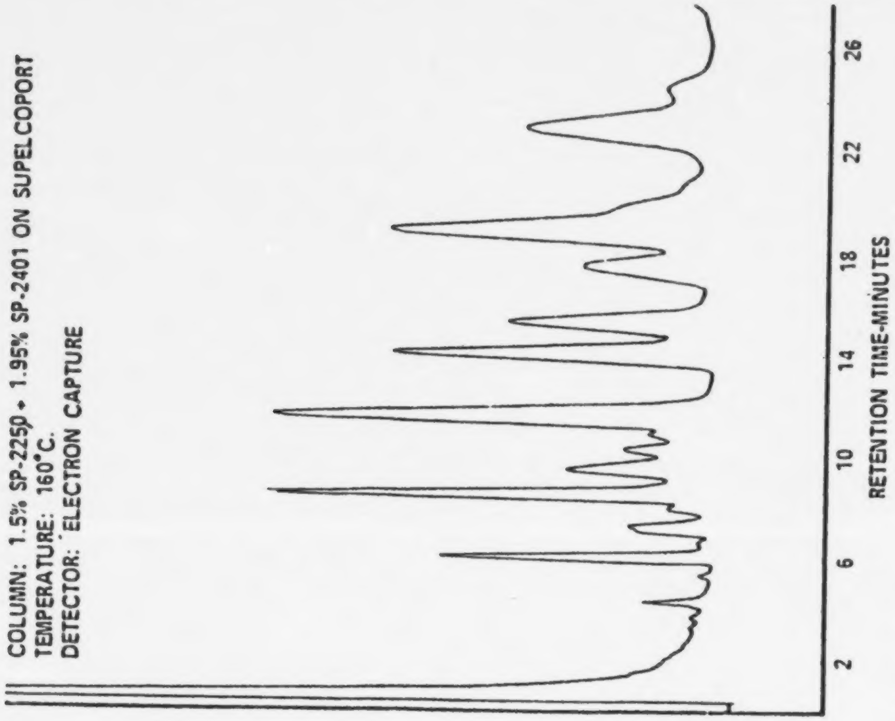
COLUMN: 1.5% SP-2250 + 1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 160°C.
DETECTOR: ELECTRON CAPTURE

Figure 8. Gas chromatogram of PCB-1248

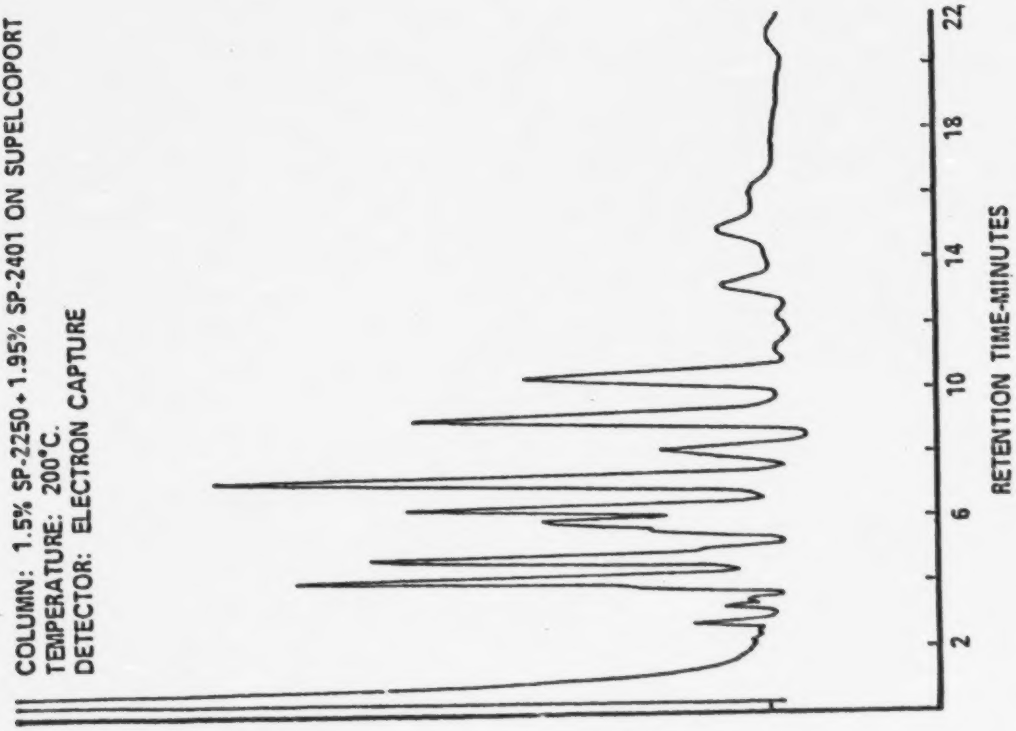

Figure 9. Gas chromatogram of PCB-1254

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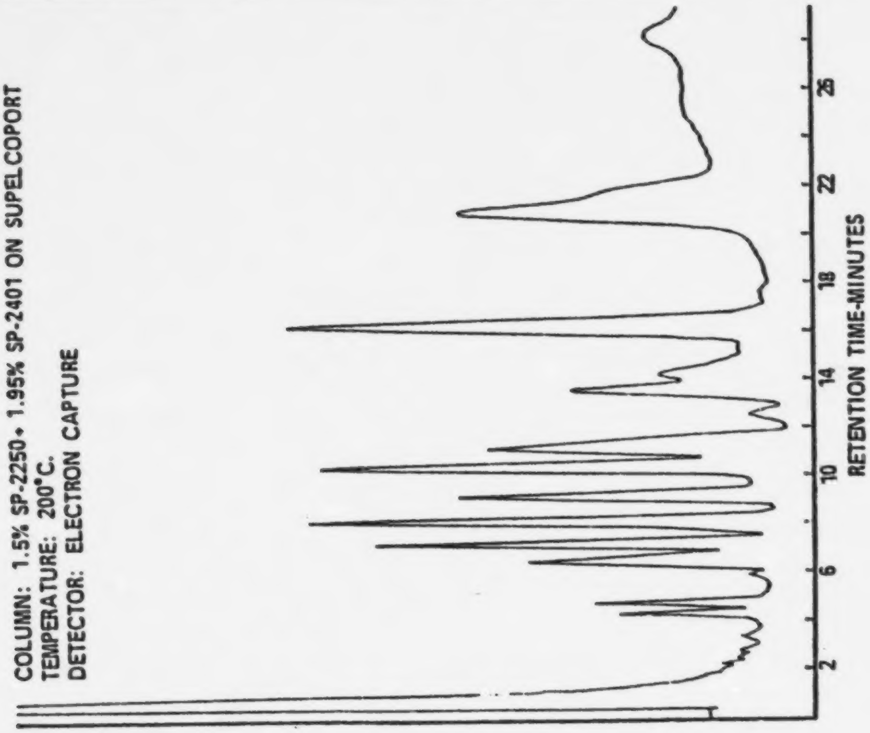

Figure 10. Gas chromatogram of PCB-1260

METHOD 624--PURGEABLES REPRODUCED FROM THE FEDERAL REGISTER, VOL. 44, No. 233, DECEMBER 3, 1979, PP. 69532-69539

Purgeables—Method 624

1. *Scope and Application.*

1.1 This method is designed to determine volatile organic materials that are amenable to the purge and trap method. The parameters listed in Table 1 may be determined by this method.

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutants Discharge Elimination System (NPDES).

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Table 2 represent sensitivities that can be achieved in wastewaters.

1.4 The GC/MS parts of this method are recommended for use only by persons experienced in GC/MS analysis or under the close supervision of such qualified persons.

1.5 The trapping and chromatographic procedures described do not apply to the very volatile pollutant, dichlorodifluoromethane. An alternative three stage trap containing charcoal is to be used if this compound is to be analyzed. See EPA Method 601 and Reference 1. Primary ion for quantitative analysis of this compound is 101. The secondary ions are 85, 87, and 103.

1.6 Although this method can be used for measuring acrolein and acrylonitrile, the purging efficiencies are low and erratic. For a more reliable quantitative analysis of these compounds, use direct aqueous injection (Ref. 4–6) or EPA Method 603, Acrolein and Acrylonitrile, EMSL, Cincinnati, Ohio.

2. *Summary of Method.*

21. A sample of wastewater is purged with a stream of inert gas. The gas is bubbled through a 5 ml water sample contained in a specially designed purging chamber. The volatile organics are efficiently transferred from the aqueous phase into the gaseous phase where they are passed through a sorbent bed designed to trap out the organic volatiles. After purging is complete, the trap is backflushed while being rapidly heated in order to thermally desorb the components into the inlet of a gas chromatograph. The components are separated via the gas chromatograph and detected using a mass spectrometer which is used to provide both qualitative and quantitative information. The chromatographic conditions as well as typical mass spectrometer operating parameters are given.

3. *Interferences.*

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. Impurities in the purge gas and organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) through the septum seal into the sample during shipment and storage. A field blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce cross contamination, it is recommended that the purging device and sample syringe be rinsed out twice, between samples, with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross-contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds, or high organohalide levels, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

4. *Apparatus and Materials.*

4.1. Sampling equipment, for discrete sampling.

4.1.1 Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry vial at 105°C for one hour before use.

4.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash and dry at 105°C for one hour before use.

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: a purging device, a trap, and a desorber. The complete device is available commercially from several vendors or can be constructed in the laboratory according to the specifications of Bellar and Lichtenberg (Ref. 2,3). The sorbent trap consists of ⅛ in. O.D. (0.105 in. I.D.) x 25 cm long stainless steel tubing packed with 15 cm of Tenax-GC (60–80 mesh) and 8 cm of Davison Type-15 silica gel (35–60 mesh). See figures 1 through 4. Ten centimeter traps may be used providing that the recoveries are comparable to the 25 cm traps.

4.3 Gas chromatograph—Analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including an analytical column.

4.3.1 Column 1—An 8 ft. stainless steel column (⅛ in. OD x 0.90 to 0.105 in. ID) packed with 1% SP–1000 coated on 60/80 mesh Carbopack B preceded by a 5-cm precolumn packed with 1% SP–1000 coated on 60/80 mesh Chromosorb W. A glass column (¼ in OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.3.2 Column 2—An 8 ft. stainless steel column (⅛ in OD x 0.09 to 0.105 in. ID) packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (⅛ in. OD x 0.09 to 0.105 in. ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. A glass column (¼ in. OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.4 Syringes—glass, 5-ml hypodermic with Luer-Lok tip (3 each).

4.5 Micro syringes—10, 25, 100 µl.

4.6 2-way syringe valve with Luer ends (3 each, Teflon or Kel-F).

4.7 Syringe—5 ml gas-tight with shut-off valve.

4.8 8-inch, 20-gauge syringe needle—One per each 5-ml syringe.

4.9 Mass Spectrometer—capable of scanning from 20–260 in six seconds or less at 70 volts (nominal), and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when injected through the GC inlet. The mass spectrometer must be interfaced with a gas chromatograph equipped with an all-glass, on-column injector system designed for packed column analysis. All sections of the transfer lines must be glass or glass-lined and deactivated. Use Sylon-CT, Supelco, (or equivalent) to deactivate. The GC/MS interface can utilize any separator that gives recognizable mass spectra (background corrected) and acceptable calibration points at the limit of detection specified for each compound in Table 2.

4.10 A computer system should be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC–MS runs. There must be computer software available to allow searching any GC/MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under a specific ion plot peak is essential for quantification.

5. *Reagents.*

5.1 Sodium thiosulfate—(ACS) Granular.

5.2 Trap Materials

5.2.1 Porous polymer packing 60/80 mesh chromatographic grade Tenax GC (2,6-diphenylene oxide).

5.2.3 Silica gel-(35–60 mesh)—

5.2.2 Three percent OV–1 on Chromosorb-W 60/80 mesh. Davison, grade-15 or equivalent.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water

5.4.1 Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water or well water through a carbon filter bed containing about 1 lb. of activated carbon.

5.4.2 A water system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

5.4.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle equipped with a Teflon seal.

5.5 Stock standards (2 mg/ml)—Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of such materials.

5.5.1 Place about 9.8 ml of methanol into a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Tare the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material:

5.5.2.1 Liquids—using a 100 µl syringe, immediately add 2 to 3 drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases—To prepare standards of bromomethane, chloroethane, chloromethane, and vinyl chloride, fill a 5-ml valved gas-tight syringe with the reference standard to the 5.0-ml mark. Lower the needle to 5 mm above the methyl alcohol menicus. Slowly inject the reference standard into the neck of the flask (the heavy gas will rapidly dissolve into the methyl alcohol).

5.5.3 Reweigh the flask, dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15-ml screw-cap bottle equipped with a Teflon cap liner.

5.5.4 Calculate the concentration in mg per ml (equivalent to µg per µl) from the net gain in weight.

5.5.5 Store stock standards at 4° C. Prepare fresh standards every second day for the four gases and 2-chloroethylvinyl ether. All other standards must be replaced with fresh standards each week.

5.6 Surrogate Standard Dosing Solution—From stock standard solutions prepared as above, add a volume to give 1000 µg each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 40 ml of organic-free water contained in a 50-ml volumetric flask, mix and dilute to volume. Prepare a fresh surrogate standard dosing solution weekly. Dose the surrogate standard mixture into every 5-ml sample and reference standard analyzed.

6. *Calibration.*

6.1 Using the stock standards, prepare secondary dilution standards of the compounds of interest, either singly or mixed together in methanol. The standards should be at concentrations such that the aqueous standards prepared in 6.2 will bracket the working range of the chromatographic system. If the limit of detection listed in Table 2 is 10 µg/l, for example, prepare secondary methanolic standards at 100 µg/l, and 500 µg/l, so that aqueous standards prepared from thee secondary calibration standards, and the primary standards, will define the linearity of the detector in the working range.

6.2 Using both the primary and secondary dilution standards, prepare calibration standards by carefully adding 20.0 µl of the standard in methanol to 100, 500, or 1000 ml of organic-free water. A 25 µl syringe (Hamilton 702N or equivalent) should be used for this operation. These aqueous standards must be prepared fresh daily.

6.3 Assemble the necessary gas chromatographic and mass spectrometer apparatus and establish operating parameters equivalent to those indicated in Table 2. By injecting secondary dilution standards, establish the linear range of the analytical system for each compound and demonstrate that the analytical system meets the limit of detection requirements in Table 2.

6.4 Assemble the necessary purge and trap device. Pack the trap as shown in Figure 2 and condition overnight at a nominal 180° C by backflushing with an inert gas flow of at least 20 ml/min. Daily, prior to use, condition the traps for 10 minutes by backflushing at 180° C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 9. Compare the responses to those obtained by injection of standards (6.3), to determine the analytical precision. The analytical precision of the analysis of aqueous standards must be comparable to data presented by Bellar and Lichtenberg (1978, Ref. 1) before reliable sample analysis may begin.

6.5 Internal Standard Method—The internal standard approach is acceptable for the purgeable organics. The utilization of the internal standard method requires the periodic determination of response factors (RF) which are defined in equation 1.

Eq. (1) $RF = (A_s C_{is})/(A_{is} C_s)$

Where:

A_s is the integrated area or peak height of the characteristic ion for the priority pollutant standard.

A_{is} is the integrated area or peak height of the characteristic ion for the internal standard.

C_{is} is the amount of the internal standard in µg.

C_s is the amount of the pollutant standard in µg.

The relative response ratio for each pollutant should be known for at least two concentration values—50 ng injected to approximate 10 µg/l and 500 ng to approximate the 100 µg/l level. Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response. The response factor (RF) must be determined over all concentration ranges of standard (C_s) which are being determined. (Generally, the amount of internal standard added to each extract is the same so that C_{is} remains constant.) This should be done by preparing a calibration curve where the response factor (RF) is plotted against the standard concentration (C_s). Use a minimum of three concentrations over the range of interest. Once this calibration curve has been determined, it should be verified daily by injecting at least one standard solution containing internal standard. If significant drift has occurred, a new calibration curve must be constructed.

Note.—EPA, through its contractors and certain of its Regional Laboratories, is currently evaluating selected compounds for use as internal standards in the analysis of organics by purge and trap.

6.6 The external standard method can also be used at the discretion of the analyst. Prepare a master calibration curve using a minimum of three standard solutions of each of the compounds that are to be measured. Plot concentrations versus integrated areas or peak heights (selected characteristic ion for GC/MS). One point on each curve should approach the method detection limit. After the master set of instrument calibration curves have been established, they should be verified daily by injecting at least one standard solution. If significant drift has occurred, a new calibration curve must be constructed.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should daily demonstrate, through the analysis of an organic-free water method blank, that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by determining the precision of the method in blank water and spiking each 5-ml sample, standard, and blank with surrogate halocarbons.

7.3.1 Determine the precision of the method by dosing blank water with the compounds selected as surrogate standards—bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane—and running replicate analyses. Calculate the recovery and its standard deviation. These compounds represent early, middle, and late eluters over the range of the pollutant compounds.

7.3.2 The sample matrix can affect the purging efficiencies of individual compounds; therefore, each sample must be dosed with the surrogate standards and analyzed in a manner identical to the internal standards in blank water. If the recovery of the surrogate standard shows a deviation greater than two standard deviations (7.3.1), repeat the dosed sample analyses. If the deviation is again greater than two standard deviations, dose another aliquot of the same sample with the compounds of interest at approximately two times the measured values and analyze. Calculate the recovery for the individual compounds using these data.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers having a total volume greater than 20 ml. Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottles so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

8.2 The sample must be iced or refrigerated from the time of collection until extraction. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 μg/40 ml) to the empty sample bottles just prior to shipping to the sample site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

8.3 All samples must be analyzed within 7 days of collection.

9. *Sample Extraction and Gas Chromatography.*

9.1 Remove standards and samples from cold storage (approximately an hour prior to an analysis) and bring to room temperature by placing in a warm water bath at 20–25°C.

9.2 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min. Attach the trap inlet to the purging device, and set the device to the purge mode. Open the syringe valve located on the purging device sample introduction needle.

9.3 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 5.0 μl of the surrogate spiking solution (7.3) through the valve bore, then close the valve.

9.4 Attach the syringe-valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber.

9.5 Close both valves and purge the sample for 12.0 ±.05 minutes.

9.6 After the 12-minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap, with an inert gas, at 20 to 60 ml/min for 4 minutes. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the initial program temperature of 45°C.

9.7 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-ml flushes of organic-free water. After the purging device has been emptied, continue to allow the purge gas to vent through the chamber until the frit is dry, and ready for the next sample.

9.8 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample. (Note: If this bake out step is omitted, the amount of water entering the GC/MS system will progressively increase causing deterioration of and potential shut down of the system.)

9.9 The analysis of blanks is most important in the purge and trap technique since the purging device and the trap can be contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with organic-free water that has been prepared by passing distilled water through a pretested activated carbon column. Blanks should be sealed, stored at 4°C, and analyzed with each group of samples.

10. *Gas Chromatography—Mass Spectrometry.*

10.1 Table 2 summarizes the recommended gas chromatographic column materials and operting conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by Column 1 is shown in Figure 5.

10.2 GC–MS Determination—Suggested analytical conditions for determination of the pollutants amenable to purge and trap, using the Tekmar LCS–1 and GC/MS are given below. Operating conditions vary from one system to another; therefore, each analyst must optimize the conditions for each purge and trap and GC/MS system.

10.3 Purge Parameters.

Sample size—5.0 ml.
Purge gas—Helium, high purity grade.
Purge time—12 minutes.
Purge flow—40 ml/min.
Trap dimensions—⅛ in. O.D. (0.105 in. I.D.)x25 cm long.
Trap sorbent—Tenax-GC, 60/80 mesh (15 cm), plus Type 15 silica gel, 35/60 mesh (8 cm).
Desorption flow—20 ml/min.
Desorption time—4 min.
Desorption temperature—180° C.

10.4 Mass Spectrometer Parameters.

Electron energy—70 volts (nominal).
Mass range—20-27, 33-260 amu.
Scan time—6 seconds or less.

10.5 Calibration of the gas chromatography-mass spectrometry (GC-MS system—Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP or BFB.

10.5.1 To use DFTPP, remove the analytical column and substitute a column more appropriate to the boiling point of the reference compound (e.g. 3% SP-2250 on Supelcoport). Inject a solution containing 50 ng DFTPP and check to insure that the performance criteria listed in Table 3 are met.

10.5.2 To use BFB, inject a solution containing 20 ng BFB and check to insure that the performance criteria listed in Table 4 are met.

10.5.3 If the system performance criteria are not met for either test, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

10.6 Analyze an internal or external calibration standard to develop response factors for each compound.

11. *Qualitative and Quantitative Determination.*

11.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and at least two other ions (if available) listed in Table 5. The criteria below must be met for a qualitative identification.

11.1.1 The characteristic ions for the compound must be found to maximize in the same or within one spectrum of each other.

11.1.2 The retention time at the experimental mass spectrum must be within ±60 seconds of the retention time of the authentic compound.

11.1.3 The ratios of the three EICP peak heights must agree within ±20% with the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analyzed through the GC-MS system or from a reference library.

11.1.4 Structural isomers that have very similar mass spectra can be explicitly identified only if the resolution between the isomers in a standard mix is acceptable. Acceptable resolution is achieved if the valley height between isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

11.2 The primary ion listed in Table 5 is to be used to quantify each compound. If the sample produces an interference for the primary ion, use a secondary ion to quantify.

11.3 For low concentrations, or direct aqueous injection of acrylonitrile and acrolein, the characteristic masses listed for the compounds in Table 5 may be used for selected ion monitoring (SIM). SIM is the use of a mass spectrometer as a substance selective detector by measuring the mass spectrometric response at one or several characteristic masses in real time.

11.4 Internal Standard Method Calculations—By adding a constant known amount of internal standard (C_{is} in µg) to every sample extract, the concentration of the pollutant (C_s) in µg/l in the sample is calculated using equation 2,

$$\text{Eq. (2)}\, C_s = \frac{(A_s)(C_{is})}{(A_{is})(RF)(V_o)}$$

Where:

V_o is the volume of the original sample in liters, and the other terms are defined as in Section 6.5. To quantify, add the internal standard to the 5.0 ml sample no more than a few minutes before purging to minimize the possibility of losses due to evaporation, adsorption, or chemical reaction. Calculate the concentration by using the previous equations with the appropriate response factor taken from the calibration curve.

11.5 Extenral Standard Method Calculations—The concentration of the unknown can be calculated from the slope and intercept of the multiple point calibration curve. The unknown concentration can be determined using equation 3.

$$\text{Eq. (3) micrograms per liter} = \text{ng/ml} = \frac{(A)}{(V_s)}$$

Where:

A = Mass of compound from calibration curve (ng/5 ml).
V_s = volume of water purged (5 ml).

11.6 An alternate external standard approach for purgeables utilizes a single point calibration. Prepare and analyze a reference standard that closely approximates the response for each component in a sample. Calculate the concentration in the sample using Equation 4.

$$\text{Eq. 4 micrograms per liter} = \frac{(A)(B)}{(C)}$$

Where:

A = area of the unknown
B = concentration of standard (µg/l)
C = area of the standard.

11.7 Report all results to two significant figures. When duplicate and spiked samples are analyzed, all data obtained should be reported. Report results in micrograms per liter without correction for recovery data.

12. *References.*

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4. ASTM Annual Standards—Water, part 31, Method D2908 "Standard Recommended Practice for Measuring Water by Aqueous-Injection Gas Chromatography."

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2. "Proceedings: Seminar on Analytical Methods for Priority Pollutants," Volume 1—Denver, Colorado, November 1977; Volume 2—Savannah, Georgia, May 1978; Volume 3—Norfolk, Virginia, March 1979; USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

Table 1

Parameter	STORET No.
Acrolein	34210
Acrylonitrile	34215
Benzene	34236
Bromomethane	34413
Bromodichloromethane	32101
Bromoform	32104
Carbon Tetrachloride	32102
Chlorobenzene	34301
Chloroethane	34311
2-Chloroethylvinyl ether	34576
Chloroform	32106
Chloromethane	34418
Dibromochloromethane	34105
1,1-Dichloroethane	34496

Table 1—Continued

Parameter	STORET No.
1,2-Dichloroethane	34531
1,1-Dichloroethene	34501
trans-1,2-Dichloroethene	34546
1,2-Dichloropropane	34541
cis-1,3-Dichloropropene	34561
trans-1,3-Dichloropropene	34561
Ethylbenzene	34371
Methylene chloride	34423
1,1,2,2-Tetrachloroethane	34516
Tetrachlorethene	34475
1,1,1-Trichloroethane	34506
1,1,2-Trichloroethane	34511
Trichloroethene	39180
Trichlorofluoromethane	34488
Toluene	34010
Vinyl chloride	39175

Table 2.—*Gas Chromatography of Organics by Purge and Trap*

Compound	Retention time (minutes)		Limit of detection [3] (μg/l)
	Col. 1 [1]	Col. 2 [2]	
chloromethane	1.50	2.10	10
bromomethane	2.17	2.50	10
vinyl chloride	2.67	2.57	10
chloroethane	3.33	2.82	10
methylene chloride	5.25	4.03	10
trichlorofluoromethane	7.18	5.14	10
1,1-dichloroethene	7.92	5.25	10
bromochloromethane (SS)	8.48	6.31	—
1,1-dichloroethane	9.30	6.48	10
trans-1,2-dichloroethene	10.06	6.81	10
chloroform	10.68	7.70	10
1,2-dichloroethane	11.40	8.29	10
1,1,1-trichloroethane	12.60	9.26	10
carbon tetrachloride	13.02	9.45	10
bromodichloromethane	13.65	10.36	10
1,2-dichloropropane	14.92	11.30	10
trans-1,3-dichloropropene	15.22	11.70	10
trichloroethene	15.80	11.98	10
dibromochloromethane	16.48	12.86	10
1,1,2-trichloroethane	16.52	12.86	10
cis-1,3-dichloropropene	16.53	12.88	10
benzene	—	12.95	10
2-chloroethylvinyl ether	18.00	13.71	10
2-bromo-1-chloropropane (SS)	—	13.82	—
bromoform	19.23	15.41	10
1,1,2,2-tetrachloroethane	21.62	17.70	10
tetrachloroethene	21.67	17.44	10
1,4-dichlorobutane (SS)	—	18.13	—
toluene	—	18.53	10
chlorobenzene	24.18	20.57	10
ethylbenzene	—	25.06	10
acrolein	—	—	[4]100
acrylonitrile	—	—	[4]100

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[1] Eight ft. stainless steel column (1/8 in OD×0.1 in. ID) packed with 1% SP-1000 coated on 60/80 mesh Carbopack B preceded by a 1 ft. stainless steel column (1/8 in. OD×0.1 in. ID) packed with 1% SP-1000 coated on 60/80 mesh Chromosorb W. (A glass column (1/4 in. OD×2 mm ID) may be substituted). Carrier gas helium at 40 ml/min. Temperature program: 3 min isothermal at 45° C, then 8°/min to 220°, hold at 220° for 15 minutes.

[2] Eight ft. stainless steel column (1/8 in. OD×0.1 in. ID) packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (1/8 in. OD×0.1 in. ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. A glass column (1/4 in. OD×2 mm ID) may be substituted. Carrier gas: helium at 40 ml/min. Temperature program: 3 min. isothermal at 60° C then 8°/min to 160°, hold at 160 until all compounds elute.

[3] This is a minimum level at which the entire system must give recognizable mass spectra and acceptable calibration points.

[4] Sensitivity refers to either this method or direct aqueous injection GC–FID (Ref. 4,5,6).

Table 3.—*DFTPP Key Ions and Ion Abundance Criteria*

Mass	Ion abundance criteria
51	30 to 60 pct of mass 198.
68	Less than 2 pct of mass 69.
70	Less than 2 pct of mass 69.
127	40 to 60 pct of mass 198.
197	Less than 1 pct of mass 198.
198	Base peak, 100 pct relative abundance.
199	5 to 9 pct of mass 198.
275	10 to 30 pct of mass 198.
365	Greater than 1 pct of mass 198.
441	Present but less than mass 443.
442	Greater than 40 pct of mass 198.
443	17 to 23 pct of mass 442.

Table 4.—*BFB Keyt Ions and Ion Abundance Criteria*

Mass	Ion abundance criteria
50	20 to 40 pct of mass 95.
75	50 to 70 pct of mass 95.
95	Base peak, 100 pct relative abundance.
96	5 to 9 pct of mass 95.
173	Less than 1 pct of mass 95.
174	70 to 90 pct of mass 95.
175	5 to 9 pct of mass 95.
176	70 to 90 pct of mass 95.
177	5 to 9 pct of mass 95.

Table 5.—*Characteristic Ions of Volatile Organics*

Compound	E I ions				Primary ion
chloromethane	50	52	—	—	50
bromomethane	94	96	—	—	94
vinyl chloride	62	64	—	—	62
chloroethane	64	66	—	—	64
methylene chloride	49	51	84	86	84
trichlorofluoromethane	101	103	—	—	101
1,1-dichloroethene	61	96	98	—	96
bromochloromethane (SS)	49	130	128	51	128
1,1-dichloroethane	63	65	83	—	63
	85	98	100	—	—
trans-1,2-dichloroethene	61	96	98	—	96
chloroform	83	85	—	—	83
1,2-dichloroethane	62	64	98	100	98
1,1,1-trichloroethane	97	99	117	119	97
carbon tetrachloride	117	119	121	—	117
bromodichloromethane	83	85	127	129	127
1,2-dichloropropane	63	65	112	114	112
trans-1,3-dichloropropene	75	77	—	—	75
trichloroethene	95	97	130	132	130
dibromochloromethane	129	127	208	206	127
cis-1,3-dichloropropene	75	77	—	—	75
1,1,2-trichloroethane	83	85	97	—	—
	99	132	134	—	97
benzene	78	—	—		78
2-chloroethylvinyl ether	63	65	106	—	106
2-bromo-1-chloropropane (SS)	77	79	156	—	77
bromoform	171	173	175	250	173
	252	254	256	—	—
tetrachloroethenbe	129	131	164	166	164
1,1,2,2-tetrachloroethane	83	85	131	133	—
	166	168	—	—	168
1,4-dichlorobutane (SS)	55	90	92	—	55
toluene	91	92	—	—	92
chlorobenzene	112	114	—	—	112
ethylbenzene	91	106	—	—	106
acrolein	26	27	55	56	56
acrylonitrile	26	51	52	53	53

BILLING CODE 6560-01-M

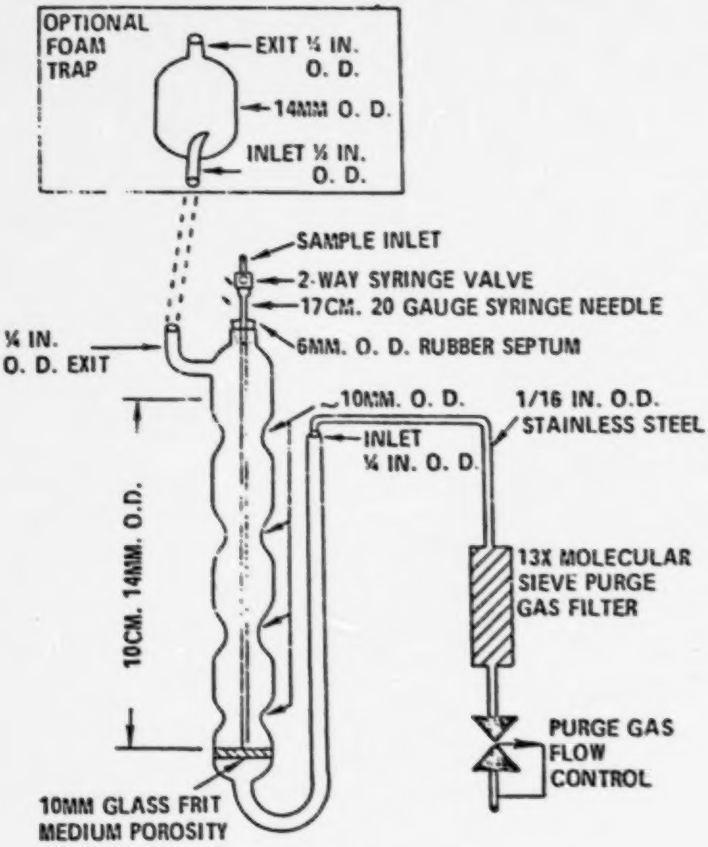

OPTIONAL FOAM TRAP
EXIT ¼ IN. O. D.
14MM O. D.
INLET ¼ IN. O. D.
SAMPLE INLET
2-WAY SYRINGE VALVE
17CM. 20 GAUGE SYRINGE NEEDLE
¼ IN. O. D. EXIT
6MM. O. D. RUBBER SEPTUM
10MM. O. D.
1/16 IN. O.D. STAINLESS STEEL
INLET ¼ IN. O. D.
10CM. 14MM. O.D.
13X MOLECULAR SIEVE PURGE GAS FILTER
PURGE GAS FLOW CONTROL
10MM GLASS FRIT MEDIUM POROSITY

Figure 1. Purging device

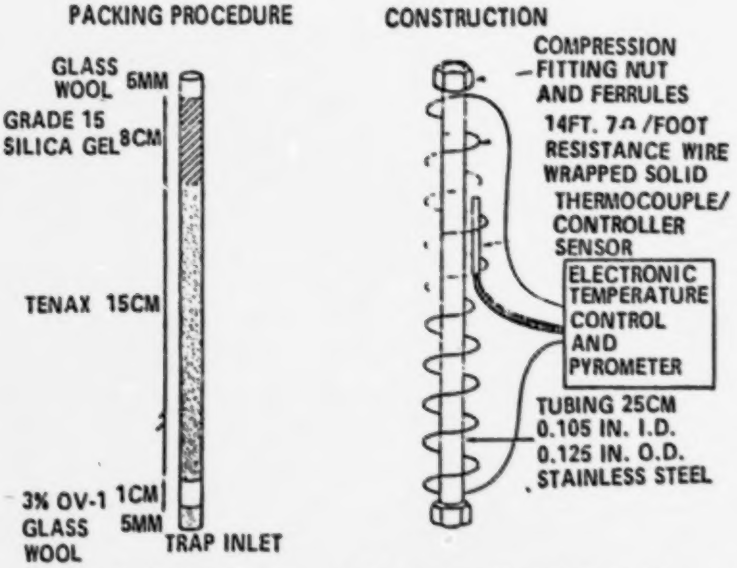

PACKING PROCEDURE
CONSTRUCTION
GLASS WOOL 5MM
GRADE 15 SILICA GEL 8CM
TENAX 15CM
3% OV-1 1CM
GLASS WOOL 5MM
TRAP INLET
COMPRESSION FITTING NUT AND FERRULES
14FT. 7Ω /FOOT RESISTANCE WIRE WRAPPED SOLID
THERMOCOUPLE/ CONTROLLER SENSOR
ELECTRONIC TEMPERATURE CONTROL AND PYROMETER
TUBING 25CM 0.105 IN. I.D. 0.125 IN. O.D. STAINLESS STEEL

Figure 2. Trap packings and construction to include desorb capability

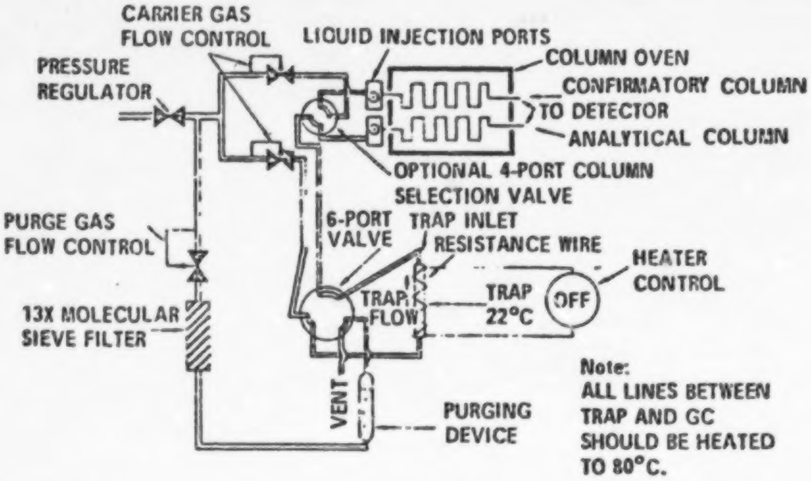

CARRIER GAS FLOW CONTROL
LIQUID INJECTION PORTS
PRESSURE REGULATOR
COLUMN OVEN
CONFIRMATORY COLUMN
TO DETECTOR
ANALYTICAL COLUMN
OPTIONAL 4-PORT COLUMN SELECTION VALVE
PURGE GAS FLOW CONTROL
6-PORT VALVE
TRAP INLET
RESISTANCE WIRE
HEATER CONTROL
13X MOLECULAR SIEVE FILTER
TRAP FLOW
TRAP 22°C
OFF
VENT
PURGING DEVICE
Note:
ALL LINES BETWEEN TRAP AND GC SHOULD BE HEATED TO 80°C.

Figure 3. Schematic of purge and trap device - purge mode

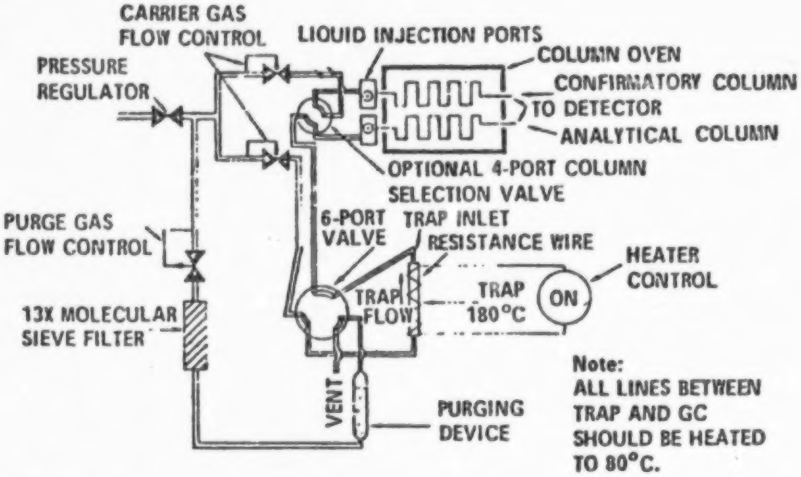

CARRIER GAS FLOW CONTROL
LIQUID INJECTION PORTS
PRESSURE REGULATOR
COLUMN OVEN
CONFIRMATORY COLUMN
TO DETECTOR
ANALYTICAL COLUMN
OPTIONAL 4-PORT COLUMN SELECTION VALVE
PURGE GAS FLOW CONTROL
6-PORT VALVE
TRAP INLET
RESISTANCE WIRE
HEATER CONTROL
13X MOLECULAR SIEVE FILTER
TRAP FLOW
TRAP 180°C
ON
VENT
PURGING DEVICE
Note:
ALL LINES BETWEEN TRAP AND GC SHOULD BE HEATED TO 80°C.

Figure 4. Schematic of purge and trap device - desorb mode

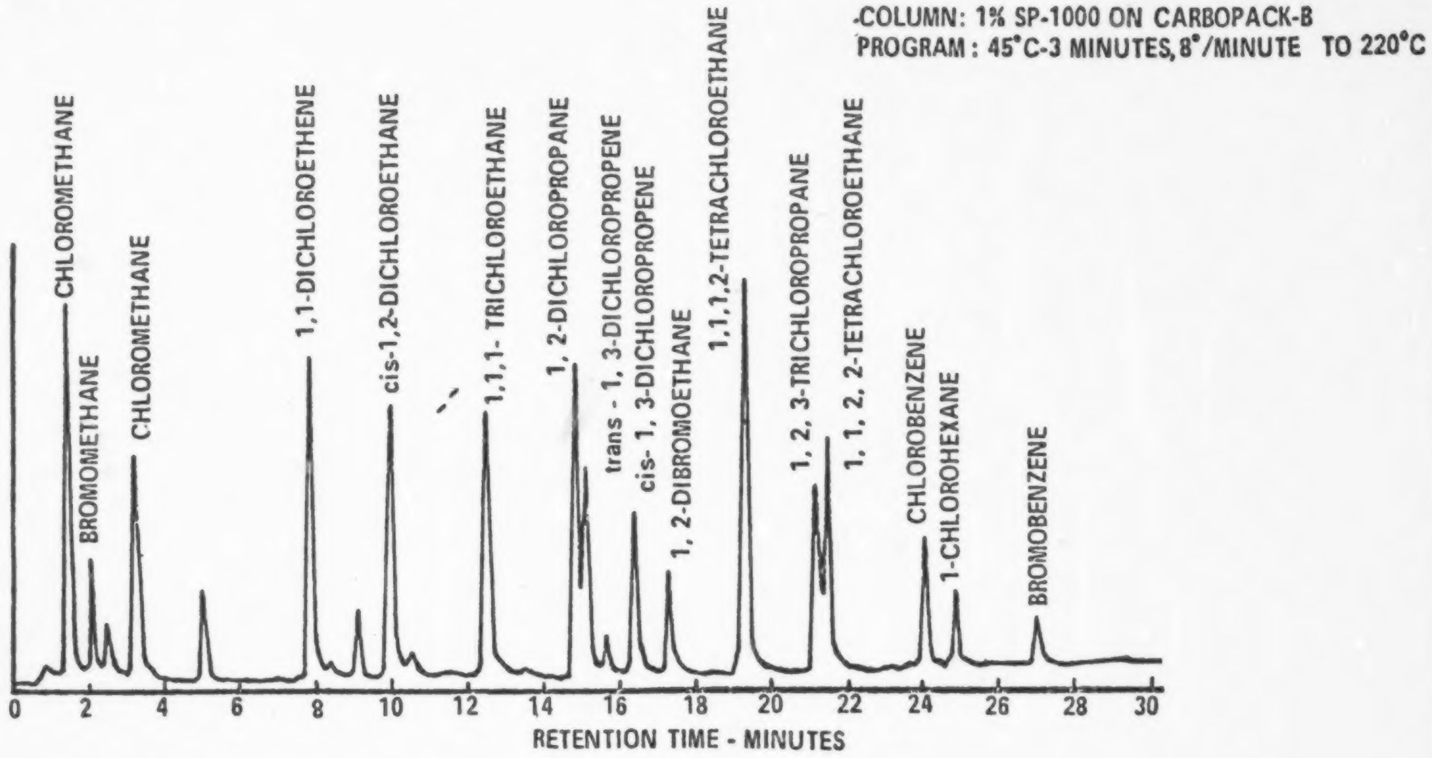


Figure 5. Gas chromatogram of volatile organics by purge and trap

BILLING CODE 6560-01-C

METHOD 625--BASE/NEUTRALS, ACIDS, AND PESTICIDES REPRODUCED FROM THE FEDERAL REGISTER, VOL. 44, No. 233, DECEMBER 3, 1979, PP. 69540-69552

Base/Neutrals, Acids, and Pesticides—Method 625

1. *Scope and Application.*

1.1 This method covers the determination of a number of organic compounds that are solvent extractable and amenable to gas chromatography. The parameters listed in Tables 1, 2 and 3 may be determined by this method.

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutants Discharge Elimination System (NPDES).

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Tables 4, 5, and 6 represent the minimum quantity that must be injected into the system to get confirmation by the mass spectrometric method described below.

1.4 The GC/MS parts of this method are recommended for use only by analysts experienced with GC/MS or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1 to 2 liter sample of wastewater is extracted with methylene chloride using separatory funnel or continuous extraction techniques. If emulsions are a problem, continuous extraction techniques should be used. The extract is dried over sodium sulfate and concentrated to a volume of 1 ml using a Kuderna-Danish (K–D) evaporator. Chromatographic conditions are described which allow for the separation of the compounds in the extract.

2.2 Quantitative analysis is performed by GC/MS using either the internal standard or external standard technique.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled.

3.3 The recommended analytical procedure may not have sufficient resolution to differentiate between certain isomeric pairs. These are anthracene and phenanthrene, chrysene and benzo(a)anthracene, and benzo(b)fluoranthene and benzo(k)fluoranthene. The GC retention time and mass spectral data are not sufficiently unique to make an unambiguous distinction between these compounds. Alternative techniques should be used to identify and quantify these specific compounds. See Reference 1.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter to 1-gallon volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to fit sample bottles. Caps must be lined with Teflon. Aluminum foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 1000 ml. Sample containers must be kept refrigerated during sampling. No plastic or rubber tubing other than Teflon may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock (Ace Glass 7228–T–72 or equivalent).

4.3 Drying column—A 20 mm ID pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

4.4 Kuderna-Danish (K–D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K–570050–1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K–57001–0500 or equivalent). Attach to concentrator tube with springs. (Kontes K–662750–0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000–0232 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K–569002–0219 or equivalent).

4.4.5 Boiling chips-extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph capable of on-column injection and all required accessories including column supplies, gases, etc.

4.6.1 Column 1—For Base/Neutral and Pesticides a 6-foot glass column (¼ in OD x 2 mm ID) packed with 3% SP–2250 coated on 100/120 Supelcoport (or equivalent).

4.6.2 Column 2—For Acids, a 6-foot glass column (¼ in OD x 2 mm ID) packed with 1% SP–1240 DA coated on 100/120 mesh Supelcoport (or equivalent).

4.7 Mass Spectrometer—Capable of scanning from 35 to 450 a.m.u. every 7 seconds or less at 70 volts (nominal) and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when the sample is introduced through the GC inlet (Reference 2). The mass spectrometer must be interfaced with a gas chromatograph equipped with an injector system designed for splitless injection and glass capillary columns or an injector system designed for on-column injection with all-glass packed columns. All sections of the transfer lines must be glass or glass-lined and must be deactivated. (Use Sylon-CT, Supelco, Inc., or equivalent to deactivate.)

Note.—Systems utilizing a jet separator for the GC effluent are recommended since membrane separators may lose sensitivity for light molecules and glass frit separators may inhibit the elution of polynuclear aromatics. Any of these separators may be used provided that it gives recognizable mass spectra and acceptable calibration points at the limit of detection specified for each individual compound listed in Tables 4, 5, and 6.

4.8 A computer system must be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC–MS runs. There must be computer software available to allow searching any GC–MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under any specific ion plot peak is essential for quantification.

4.9 Continuous liquid-liquid extractors—Teflon or glass connecting joints and stopcocks, no lubrication. (Hershberg-Wolf Extractor—Ace Glass Co., Vineland, N.J. P/N 6841–10 or equivalent).

5. *Reagents.*

5.1 Sodium hydroxide—(ACS) 6N in distilled water.

5.2 Sulfuric acid—(ACS) 6N in distilled water.

5.3 Sodium sulfate—(ACS) granular anhydrous (rinsed with methylene chloride (20 ml/g) and conditioned at 400° C for 4 hrs.).

5.4 Methylene chloride—Pesticide quality or equivalent.

5.5 Stock standards—Obtain stock standard solutions at a concentration of 1.00 μg/μl. For example, dissolve 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and dilute to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to 15 ml Teflon lined screw cap vials, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them. Protect PNA standards from light.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations that will bracket the working range of the chromatographic system (two or more orders of magnitude are suggested). If the limit of detection (Tables 4, 5, or 6) can be calculated as 20 ng injected, for example, prepare standards at 1 μg/ml, 10 μg/ml, 100 μg/ml, etc. so that injections of 1–5 μl of the calibration standards will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Tables 4, 5, and 6. By injecting calibration standards, establish the linear range of the analytical system and demonstrate that the analytical system meets the limits of detection requirements of Tables 4, 5, and 6. If the sample gives peak areas above the working range, dilute and reanalyze.

6.3 Internal Standard Method—The internal standard approach is acceptable for all of the semivolatile organics. The utilization of the internal standard method requires the periodic determination of response factors (RF) which are defined in equation 1.

Eq. 1 $RF=(A_s C_{is})/(A_{is} C_s)$

Where:

A_s is the integrated area or peak height of the characteristic ion for the pollutant standard.

A_{is} is the integrated area or peak height of the characteristic ion for the internal standard.

C_{is} is the amount (μg) of the internal standard.

C_s is the amount (μg) of the pollutant standard.

6.3 The relative response ratio for the pollutants should be known for at least two concentration values—20 ng injected to approximate 10 μg/l and 200 ng injected to approximate the 100 μg/l level. (Assuming 1 ml final volume and a 2 μl injection). Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response.

The response factor (RF) should be determined over all concentration ranges of standard (C_s) which are being determined. (Generally, the amount of internal standard added to each extract is the same (20 μg) so that C_{is} remains constant.) This should be done by preparing a calibration curve where the response factor (RF) is plotted against the standard concentration (C_s), using a minimum of three concentrations over the range of interest. Once this calibration curve has been determined, it should be verified daily by injecting at least one standard solution containing internal standard. If significant drift has occurred, a new calibration curve must be constructed. To quantify, add the internal standard to the concentrated sample extract no more than a few minutes before injecting into the GC/MS to minimize the possibility of losses due to evaporation, adsorption, or chemical reaction. Calculate the concentration by using the previous equations with the appropriate response factor taken from the calibration curve. Either deuterated or fluorinated compounds can be used as internal standards and surrogate standards. Naphthalene-d_8, anthracene-d_{10}, pyridine-d_5, aniline-d_5, nitrobenzene-d_5, 1-fluoronaphthalene, 2-fluoronaphthalene, 2-fluorobiphenyl, 2,2′-difluorobiphenyl, and 1,2,3,4,5-pentafluorobiphenyl have been used or suggested as appropriate internal standards/surrogates for the base-neutral compounds. Phenol-d_6, pentafluorophenol, 2-perfluoromethyl phenol, and 2-fluorophenol have been used or suggested for the acid compounds. Compounds used as internal standards are not to be used as surrogate standards. The internal standard must be different from the surrogate standards.

6.5 The external standard method can also be used at the discretion of the analyst. Prepare a master calibration curve using a minimum of three standard solutions of each of the compounds that are to be measured. Plot concentrations versus integrated areas or peak heights (selected characteristic ion for GC/MS). One point on each curve should approach the limit of detection (Tables 4, 5, and 6). After the master set of instrument calibration curves have been established, they should be verified daily by injecting at least one standard solution. If significant drift has occurred, a new calibration curve must be constructed.

7. *Quality Control.*

7.1 Before processing any samples, demonstrate through the analysis of a method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected and analyzed to determine the precision of the sampling technique. Laboratory replicates should be analyzed to determine the precision of the analysis. Fortified samples should be analyzed to determine the accuracy of the analysis. Field blanks should be analyzed to check for contamination introduced during sampling and transportation.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, they must be preserved as follows:

8.2.1 If the sample contains residual chlorine, add 35 mg of sodium thiosulfate per 1 ppm of free chlorine per liter of sample.

8.2.2 Adjust the pH of the water sample to a pH of 7 to 10 using sodium hydroxide or sulfuric acid. Record the volume of acid or base used.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction (Base/Neutrals, Acids, and Pesticides).*

9.1 Samples may be extracted by separatory funnel techniques or with a continuous extractor as described in Section 10. Where emulsions prevent acceptable solvent recovery with the separatory funnel technique, the analyst must use the continuous extractor.

9.2 The details of the extraction technique should be adjusted according to the sample volume. The technique described below assumes a sample volume of 1000 ml. For volumes approximating 2-liters, the volume of extraction solvent should be adjusted to 250, 100, and 100 ml for the serial extraction of the base neutrals, and 200, 100, and 100 ml for the acids.

9.3 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Adjust the pH of the sample with 6N NaOH to 11 or greater. Use multirange pH paper for the measurements. Proceed to Section 10 if continuous extraction is used.

9.4 Add 60 ml methylene chloride to the sample bottle, cap, and shake 30 seconds to rinse the walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release excess vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. (If the emulsion cannot be broken, that is, recovery is less than 80% of the added solvent corrected for the water solubility of methylene chloride, transfer the sample, solvent, and emulsion into a continuous extractor and proceed as described in Section 10). Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.5 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.6 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K–D flask equipped with 10 ml concentrator tube. Rinse the Erlenmeyer with 20 to 40 ml of methylene chloride. Pour this through the drying column. Seal, label as base/neutral fraction, and proceed with the acid extraction. If the extract must be stored overnight before analysis by GC/MS, it may be transferred to a 2 ml serum vial equipped with a Teflon-lined rubber septum and crimp cap.

9.7 Acid (Phenols) Extraction—Adjust the pH of the water, previously extracted for base-neutrals, with 6N H_2SO_4 to 2 or below. Serially extract with 60, 60 and 60 ml portions of distilled-in-glass methylene chloride. Collect and combine the extracts in a 250-ml Erlenmeyer flask then dry by passing through a column of anhydrous sodium sulfate. Rinse the Erlenmeyer with 20 to 40 ml of methylene chloride and pour through the drying column. Seal, label acid fraction and prepare for concentration.

9.8 Concentrate the extracts (Base/Neutrals and Acids) in a 500 ml K–D flask equipped with a 10 ml concentrator tube.

9.9 Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro-Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride through the top. Place the K–D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water, and the entire lower rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume 1 ml, remove the K–D apparatus and allow the solvent to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of methylene chloride. A 5-ml syringe is recommended for this operation.

9.10 Add a clean boiling chip and attach a two-ball micro-Snyder column to the concentrator tube in 9.8. Prewet the column by adding about 0.5 ml methylene chloride through the top. Place the K–D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5–10 minutes. At the proper rate of distillation the balls of the column actively chatter but the chambers do not flood. When the liquid reaches an apparent volume of about 0.5 ml, remove the K–D from the water bath and allow the solvent to drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with approximately 0.2 ml of methylene chloride. Adjust the final volume to 1.0 ml, seal, and label as acid fraction.

9.11 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. *Emulsions/Continuous Extraction.*

10.1 Place 100 to 150 ml of methylene chloride in the extractor and 200–500 ml methylene chloride in the distilling flask.

10.2 Add the aqueous sample (pH 11 or greater) to the extractor. Add blank water as necessary to operate the extractor and extract for 24 hours. Remove the distilling flask and pour the contents through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Collect the methylene chloride in a 500 ml K–D evaporator flask quipped with a 10 ml concentrator tube. Seal, label as the base/neutral fraction, and concentrate as per sections 9.8 to 9.10.

10.3 Adjust the pH of the sample in the continuous extractor to 2 or below using 6N sulfuric acid. Charge a clean distilling flask with 500 ml of methylene chloride. Extract for 24 hours. Remove the distilling flask and pour the contents through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Collect the methylene chloride layer on a K–D evaporator flask equipped with a 10 ml concentrator tube. Label as the acid fraction. Concentrate as per sections 9.8 to 9.10.

11. *Calibration of the GC–MS System.*

11.1 At the beginning of each day, the mass calibration of the GC–MS system must be checked and adjusted if necessary to meet DFTPP specifications (11.3). Each day base-neutrals are measured, the column performance specification (12.1) with benzidine must be met. Each day the acids are measured, the column performance specification (13.1) with pentachlorophenol must be met. DFTPP can be mixed in solution with either of these compounds to complete two specifications with one injection, if desired.

11.2 To perform the mass calibration test of the GC–MS system, the following instrumental parameters are required:

Electron energy—70 volts (nominal).
Mass range—35 to 450 a.m.u.
Scan time—7 seconds or less.

11.3 GC–MS system calibration—Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP. Inject a solution containing 50 ug DFTPP and check to insure that performance criteria listed in Table 10 are met. If the system performance criteria are not met, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

12. *Gas Chromatography-Mass Spectrometry of Base/Neutral Fraction.*

12.1 At the beginning of each day that base/neutral analyses are to be performed, inject 100 nanograms of benzidine either separately or as part of a standard mixture that may also contain 50 ng of DFTPP. The tailing factor for benzidine should be less than 3. Calculation of the tailing factor is given in Reference 2 and described in Figure 8.

12.2 Establish chromatographic conditions equivalent to those in Tables 4 and 5. Included in these tables are estimated retention times and sensitivities that can be achieved by this method. Examples of the separatioins achieved by these columns are shown in Figures 1 and 3 through 7.

12.3 Program the GC/MS to operate in the Extracted Ion Current Profile (EICP) mode, and collect EICP for the three ions listed in Tables 7 and 8 for each compound being measured. Operating in this mode, calibrate the system response for each compound as described in Section 6, using either the internal or external standard procedure.

12.4 If the internal standard approach is being used, the analyst may not add the standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

12.5 Inject 2 to 5 μl of the sample extract. The solvent-flush technique is preferred. If external calibration is employed, record the volume injected to the nearest 0.05 μl. If the response for any ion exceeds the linear range of the system, dilute the extract and reanalyze.

12.6 Qualitative and quantitative measurements are made as described in Section 14. When the extracts are not being used for analysis, store them in vials with unpierced septa in the dark at 14° C.

13. *Gas Chromatography/Mass Spectrometry of Acid Fraction.*

13.1 At the beginning of each day that acid fraction analyses are to be performed, inject 50 nanograms of pentachlorophenol either separately or as part of a standard mixture that may also contain DFTPP. The tailing factor for pentachlorophenol should be less than 5. Calculation of the tailing factor is given in Reference 2 and described in Figure 8.

13.2 Establish chromatographic conditions equivalent to those in Table 6. Included in this table are estimated retention times and sensitivities that can be achieved by this method. An example of the separation achieved by the column is shown in Figure 2.

13.3 Program the GC/MS to operate in the Extracted Ion Current Profile mode, and collect EICP for the three ions listed in Table 9 for each phenol being measured. Operating in this mode, calibrate the system response for each compound as described in Section 6 using either the internal or external standard procedure.

13.4 If the internal standard approach is being used, the analyst may not add the standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

13.5 Inject 2 to 5 μl of the sample extract. The solvent-flush technique is preferred. If external standard calibration is employed, record the volume injected to the nearest 0.05 μl. If the response for any ion exceeds the linear range of the system, dilute the extract and reanalyze.

13.6 Qualitative and quantitative measurements are made as described in Section 14. When the extracts are not being used for analysis, store them in vials with unpierced septa in the dark at 4° C.

14. *Qualitative and Quantitative Determination.*

14.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and the two other ions listed in Tables 7, 8, or 9. The criteria below must be met for a qualitative identification.

14.1.1 The characteristic ions for the compound must be found to maximize in the same or within one spectrum of each other.

14.1.2 The retention time at the experimental mass spectrum must be within ±60 seconds of the retention time of the authentic compound.

14.1.3 The ratios of the three EICP peak heights must agree within ±20% with the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analyzed through the GC–MS system or from a reference library.

14.1.4 Structural isomers that have very similar mass spectra can be explicitly identified only if the resolution between the isomers in a standard mix is acceptable. Acceptable resolution is achieved if the valley height between isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.2 In samples that contain an inordinate number of interferences the chemical ionization (CI) mass spectrum may make identification easier. In Tables 7 and 8 characteristic CI ions for most of the compounds are given. The use of chemical ionization MS to support EI is encouraged but not required.

14.3 When a compound has been identified, the quantification of that compound will be based on the integrated area from the specific ion plot of the first listed characteristic ion in Tables 7, 8 and 9. If the sample produces an interference for the first listed ion, use a secondary ion to quantify. Quantification will be done by the external or internal standard method.

14.4 Internal Standard—By adding a constant known amount of internal standard (C_{is} in μg) to every sample extract, the concentration of pollutant (C_o) is μg/l in the sample is calculated using equation 2.

$$\text{Eq. 2} \qquad C_o = \frac{(A_s)\ (C_{is})}{(A_{is})\ (RF)\ (Vo)}$$

Where: V_o is the volume of the original sample in liters, and the other terms are defined as in Section 6.3.

14.5 External Standard—The concentration of the unknown can be calculated from the slope and intercept of the calibration curve. The unknown concentration can be determined using equation 3.

Eq. 3

$$\text{Micrograms/liter} = \text{ng/ml} = \frac{(A)(V_t)}{(V_i)(V_s)}$$

where:

A = mass of compound from calibration curve (ng).

V_i = volume of extract injected (μl).

V_t = volume of total extract (μl).

V_s = volume of water extracted (ml).

14.6 Report all results to two significant figures. Report results in micrograms per liter (Base/Neutrals and Acids) without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

14.7 In order to minimize unnecessary GC–MS analysis of method blanks and field blanks, the field blank may be screened on a FID–GC equipped with the appropriate SP–2250 or SP–1240 DA columns.

15. **References**

1. Method 610, Polynuclear Aromatic Hydrocarbons, EMSL, Cincinnati, Ohio 45268, 1979.
2. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography—Mass Spectrometry Systems," J. W. Eichelberger, L. E. Harris and W. L. Budde, *Anal. Chem. 47*, 995–1000 (1975).

Bibliography

1. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," March 1977 (revised April 1977). USEPA, Effluent Guidelines Division, Washington, D.C. 20460.
2. "Proceedings—Seminar on Analytical Methods for Priority Pollutants":
   Volume 1—Denver, Colorado, November 1977
   Volume 2—Savannah, Georgia, May 1978
   Volume 3—Norfolk, Virginia, March 1979
   USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

Table 1.—*Base-Neutral Extractables*

Compound	STORET No.
Acenaphthene	34205
Acenaphthylene	34200
Anthracene	34220
Benzo(a)anthracene	34526
Benzo(b)fluoranthene	34230
Benzo(k)fluoranthene	34242
Benzo(a)pyrene	34247
Benzo(g,h,i)perylene	34521
Benzidine	39120
Bis(2-chloroethyl)ether	34273
Bis(2-chloroethoxy)methane	34278
Bis(2-ethylhexyl)phthalate	39100
Bis(2-chloroisopropyl)ether	34283
4-Bromophenyl phenyl ether	34636
Butyl benzyl phthalate	34292
2-Chloronaphthalene	34581
4-Chlorophenyl phenyl ether	34641
Chrysene	34320
Dibenzo(a,h)anthracene	34556
Di n-butylphthalate	39110
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
1,2-Dichlorobenzene	34536
3,3'-Dichlorobenzidine	34631
Diethylphthalate	34336
Dimethylphthalate	34341
2,4-Dinitrotoluene	34611
2,6-Dinitrotoluene	34626
Dioctylphthalate	34596
1,2-Diphenylhydrazine	34346
Fluoranthane	34376
Fluorene	34381
Hexachlorobenzene	39700
Hexachlorobutadiene	34391
Hexachloroethane	34396
Hexachlorocyclopentadiene	34386
Indeno(1,2,3-cd)pyrene	34403
Isophorone	34408
Naphthalene	39250
Nitrobenzene	34447
N-Nitrosodimethylamine	34438
N-Nitrosodi-n-propylamine	34428
N-Nitrosodiphenylamine	34433
Phenanthrene	34461
Pyrene	34469
2,3,7,8-Tetrachlorodibenzo-p-dioxin	34675
1,2,4-Trichlorobenzene	34551

Table 2.—*Acid Extractables*

Compound	STORET No.
4-Chloro-3-methylphenol	34452
2-Chlorophenol	34586
2,4-Dichlorophenol	34601
2,4-Dimethylphenol	34606
2,4-Dinitrophenol	34616
2-Methyl-4,6-dinitrophenol	34657
2-Nitrophenol	34591
4-Nitrophenol	34646
Pentachlorophenol	39094
Phenol	34694
2,4,6-Trichlorophenol	34621

Table 3.—*Pesticide Extractables*

Compound	STORET No.
Aldrin	39330
a-BHC	39337
b-BHC	39338
d-BHC	39340
g-BHC	34259
Chlordane	39350
4,4'-DDD	39310
4,4'DDE	39320
4,4'DDT	39300
Dieldrin	39380
Endosulfan I	34361
Endosulfan II	34356
Endosulfan Sulfate	34351
Endrin	39390
Endrin Aldehyde	34366
Heptachlor	39410
Heptachlor Epoxide	39420
Toxaphene	39400
PCB-1016	34671
PCB-1221	39488
PCB-1232	39492
PCB-1242	39496
PCB-1248	39500
PCB-1254	39504
PCB-1260	39508

Table 4—*Gas Chromatography of Base/Neutral Extractables*

Compound	Retention time # (min.)	Limit of detection ##	
		ng injected	µg/1
1,3-Dichlorobenzene	7.4	20	10
1,4-Dichlorobenzene	7.8	20	10
Hexachloroethane	8.4	20	10
Bis(2-chloroethyl)ether	8.4	20	10
1,2-Dichlorobenzene	8.4	20	10
Bis(2-chloroisoprooyl)ether	9.3	20	10
N-nitroso-di-n-propyl amine		20	10
Nitrobenzene	11.1	20	10
Hexachlorobutadiene	11.4	20	10
1,2,4-Trichlorobenzene	11.6	20	10
Isophorone	11.9	20	10
Naphthalene	12.1	20	10
Bis(2-chloroethoxy) methane	12.2	20	10
Hexachlorocyclopentadiene	13.9	20	10
2-Chloronaphthalene	15.9	20	10
Acenaphthylene	17.4	20	10
Acenaphthene	17.8	20	10
Dimethyl phthalate	18.3	20	10
2,6-Dinitrotoluene	18.7	20	10
Fluorene	19.5	20	10
4-Chlorophenyl phenyl ether	19.5	20	10
2,4-Dinitrotoluene	19.8	20	10
1,2-Diphenyl hydrazine*	20.1	20	10
Diethyl phthalate	20.1	20	10
N-nitrosodiphenyl amine**	20.5	20	10
Hexachlorobenzene	21.0	20	10
4-Bromophenyl phenyl ether	21.2	20	10
Phenanthrene	22.8	20	10
Anthracene	22.8	20	10
Di-n-butyl phthalate	24.7	20	10
Fluoranthene	26.5	20	10
Pyrene	27.3	20	10
Benzidine	28.8	20	10
Butyl benzyl phthalate	29.9	20	10
Bis(2-ethylhexyl) phthalate	30.6	20	10
Chrysene	31.5	20	10
Benzo(a)anthracene	31.5	20	10
3,3'-Dichlorobenzidine	32.2	20	10
Di-n-octyl phthalate	32.5	20	10
Benzo(b)fluoranthene	34.9	20	10
Benzo(k)fluoranthene	34.9	20	10
Benzo(a)pyrene	36.4	20	10
Indeno(1,2,3-c,d)pyrene	42.7	50	25
Dibenzo(a,h)anthracene	43.2	50	25
Benzo(g,h,i)perylene	45.1	50	25
N-Nitrosodimethylamine			
Bis(chloromethyl)ether			
2,3,7,8-Tetrachlorodibenzo-p-dioxin			

#Six foot glass column (¼ in. OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: Isothermal for 4 minutes at 50° C, then 8° per min to 270° C. Hold at 270° C for 30 minutes. If desired, capillary or SCOT columns may be used.

##This is a minimum level at which the entire analytical system must give mass spectral confirmation. (Nanograms injected is based on a 2 µl injection of a one liter sample that has been extracted and concentrated to a volume of 1.0 ml.)

*Detected as azobenzene.

**Detected as diphenylamine.

Table 5.—*Gas Chromatography of Pesticide Extractables*

Compound	Retention time (min)*	Limit of detection#	
		ng injected	µg/l
a-bhc	21.1	40	10
g-bhc	22.4	40	10
b-bhc	23.4	40	10
Heptachlor	23.4	40	10
d-bhc	23.7	40	10
Aldrin	24.0	40	10
Heptachlor epoxide	25.6	40	10
Endosulfan I	26.4	40	10
Dieldrin	27.2	40	10
4,4'-DDE	27.2	40	10
Endrin	27.9	40	10
Endosulfan II	28.6	40	10
4,4'-DDD	28.6	40	10
4,4'-DDT	29.3	40	10
Endosulfan sulfate	29.8	40	10
Chlordane	19 to 30		
Toxaphene	25 to 34		
PCB-1242	20 to 32		
PCB-1254	23 to 32		

*6 foot glass column (¼ in. OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: Isothermal for 4 minutes at 50° C, then 8° per minute to 270°. Hold at 270° C for 30 minutes. If desired, capillary or SCOT columns may be used.

#This is a minimum level at which the entire analytical system must give mass spectral confirmation. (Nanograms injected is based on a 4 µl injection of a one-liter sample that has been extracted and concentrated to a volume of 1.0 ml.

Table 6.—*Gas Chromatography of Acid Extractables*

Compound	Retention time* (min)	Limit of detection#	
		ng injected	µg/l
2-Chlorophenol	5.9	50	25
2-Nitrophenol	6.4	50	25
Phenol	8.0	50	25
2,4-Dimethylphenol	9.4	50	25
2,4-Dichlorophenol	9.8	50	25
2,4,6-Trichlorophenol	11.8	50	25
4-Chloro-3-methylphenol	13.2	50	25
2,4-Dinitrophenol	15.9	500	250

Table 6.—*Gas Chromatography of Acid Extractables*—Continued

Compound	Retention time* (min)	Limit of detection#	
		ng injected	µg/l
2-Methyl-4,6-dinitrophenol	16.2	500	250
Pentachlorophenol	17.5	50	25
4-Nitrophenol	20.3	50	25

*6 foot glass column (¼ in. OD x 2 mm ID) Packed with 1% SP-1240 DA coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: 2 min isothermal at 70°, then 8° per min to 200° C. If desired, capillary or SCOT columns may be used.

#This is a minimum level at which the entire analytical system must give mass spectral confirmation. (Nanograms injected is based on a 2 µl injection of a one liter sample that has been extracted and concentrated to 1.0 ml.)

Table 7.—*Base/Neutral Extractables Characteristic Ions*

Compound	Characteristic ions					
	Electron impact			Chemical ionization (methane)		
1,3-Dichlorobenzene	146	148	113	146	148	150
1,4-Dichlorobenzene	146	148	113	146	148	150
Hexachloroethane	117	201	199	199	201	203
Bis(2-chloroethyl) ether	93	63	95	63	107	109
1,2-Dichlorobenzene	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether	45	77	79	77	135	137
N-Nitrosodipropyl amine	130	42	101			
Isophorone	82	95	138	139	167	178
Nitrobenzene	77	123	65	124	152	164
Hexachlorobutadiene	225	223	227	223	225	227
1,2,4-Trichlorobenzene	180	182	145	181	183	209
Naphthalene	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	93	95	123	65	107	137
Hexachlorocyclopentadiene	237	235	272	235	237	239
2-Chloronaphthalene	162	164	127	163	191	203
Acenaphthylene	152	151	153	152	153	181
Acenaphthene	154	153	152	154	155	183
Dimethyl phthalate	63	194	164	151	163	164
2,6-Dinitrotoluene	165	63	121	63	211	223
Fluorene	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	204	206	141			
2,4-Dinitrotoluene	165	89	163	183	211	223
1,2-Diphenylhydrazine[1]	77	93	105	185	213	225
Diethylphthalate	149	177	150	177	223	251
N-Nitrosodiphenylamine[2]	169	168	167	169	170	198
Hexachlorobenzene	284	142	249	284	286	288
4-Bromophenyl phenyl ether	248	250	141	249	251	277
Phenanthrene	178	179	176	178	179	207
Anthracene	178	179	176	178	179	207
Dibutyl phthalate	149	150	104	149	205	279
Fluoranthene	202	101	100	203	231	243
Pyrene	202	101	100	203	231	243
Benzidine	184	92	185	185	213	225
Butyl benzyl phthalate	149	91		149	299	327
Bis(2-ethyl hexyl) phthalate	149	167	279	149		
Chrysene	228	226	229	228	229	257
Benzo(a)anthracene	228	229	226	228	229	257
3,3'-Dichlorobenzidine	252	254	126			
Dioctyl phthalate	149					
Benzo(b)fluoranthene	252	253	125	252	253	281
Benzo(k)fluoranthene	252	253	125	252	253	281
Benzo(a)pyrene	252	253	125	252	253	281
Indeno(1,2,3-c,d)pyrene	276	138	277	276	277	305
Dibenzo(a,h)anthracene	278	139	279	278	279	307
Benzo(g,h,i)perylene	276	138	277	276	277	305
N-nitrosodimethyl amine	42	74	44			
Bis(chloromethyl) ether	45	49	51			
2,3,7,8-Tetrachlorodibenzo-p-dioxin		322	320	59		
Deuterated anthracene(d-10)[3]	188	94	80	189	217	

[1] Detected as azobenzene.

[2] Detected as diphenylamine.

[3] Suggested internal standard.

Table 8.—*Pesticides Characteristic Ions*

Compound	Characteristic ions electron impact		
a-BHC	183	181	109
g-BHC	183	181	109
b-BHC	181	183	109
heptachlor	100	272	274
d-BHC	183	109	181
aldrin	66	263	220
heptachlor epoxide	353	355	351
endosulfan I	201	283	278
dieldrin	79	263	279
4,4'-DDE	246	248	176
4,4'-DDD	235	165	237
endrin	81	263	82
endosulfan II	201	283	278
4,4'-DDT	235	237	165
endosulfan sulfate	272	387	422
chlordane [1]	373	375	377
toxaphene [2]	231	233	235
PCB-1242 [2]	224	260	294
PCB-1254 [2]	294	330	362

[1] Characteristic of alpha and gamma forms of chlordane.
[2] These compounds are mixtures of various isomers.

Table 9.—*Acid Extractable Characteristic Ions*

Compound	Characteristic ions					
	Electron impact			Chemical ionization (methane)		
2-Chlorophenol	128	64	130	129	131	157
2-Nitrophenol	139	65	109	140	168	122
Phenol	94	65	66	95	123	135
2,4-Dimethylphenol	122	107	121	123	151	163
2,4-Dicholorphenol	162	164	98	163	165	167
2,4,6-Trichlorophenol	196	198	200	197	199	201
4-Chloro-3-methyl phenol	142	107	144	143	171	183
2,4-Dinitrophenol	184	63	154	185	213	225
2-Methyl-4,6-dinitrophenol	198	182	77	199	227	239
Pentachlorophenol	266	264	268	267	265	269
4-Nitrophenol	65	139	109	140	168	122
Anthracene (d-10) [1]	188	94	80	189	217	....

[1] Suggested internal standard.

Table 10.—*DFTPP Key Ions and Ion Abundance Criteria*

	Ion abundance criteria
Mass:	
51	30 to 60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40 to 60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5 to 9 percent of mass 198.
275	10 to 30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17 to 23 percent of mass 442.

BILLING CODE 6560-01-M

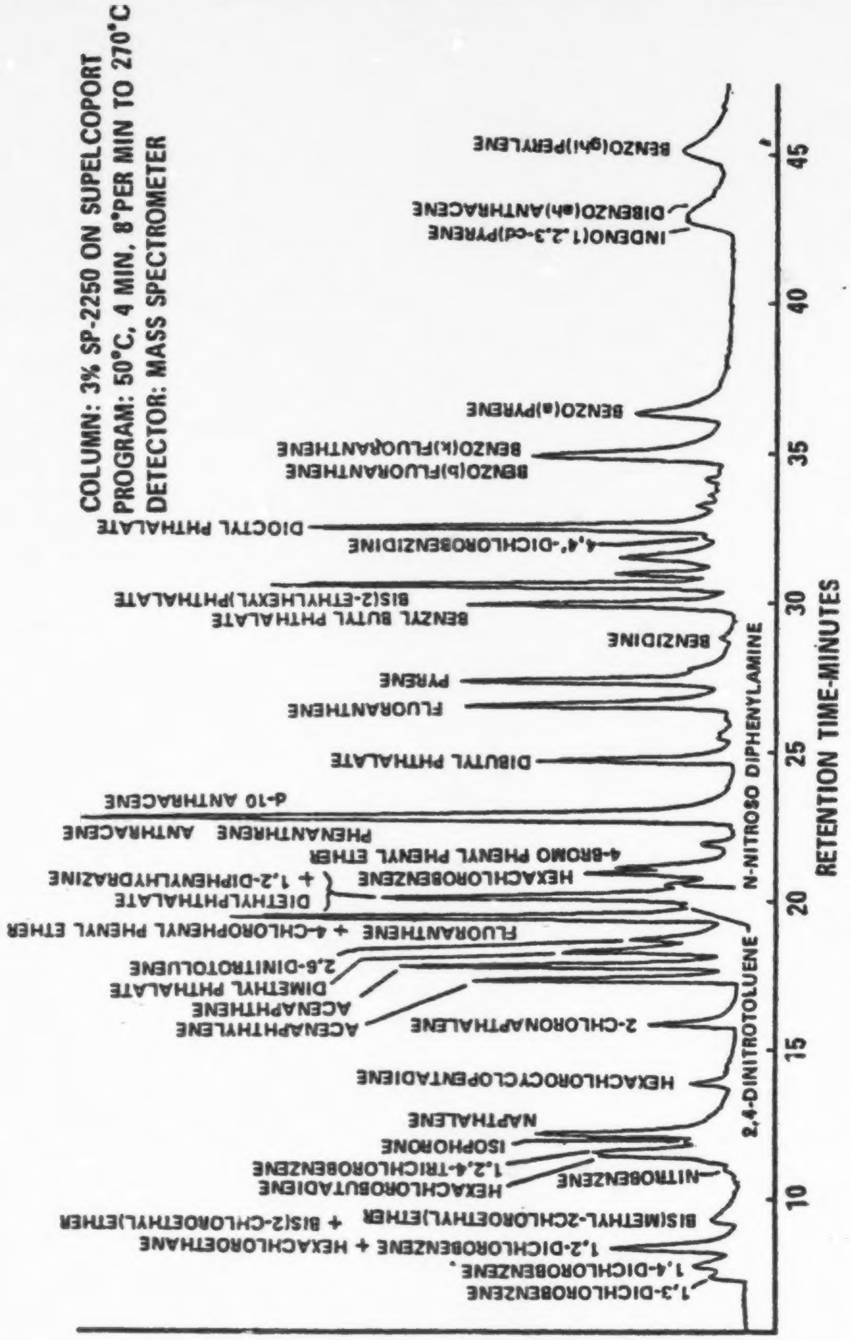
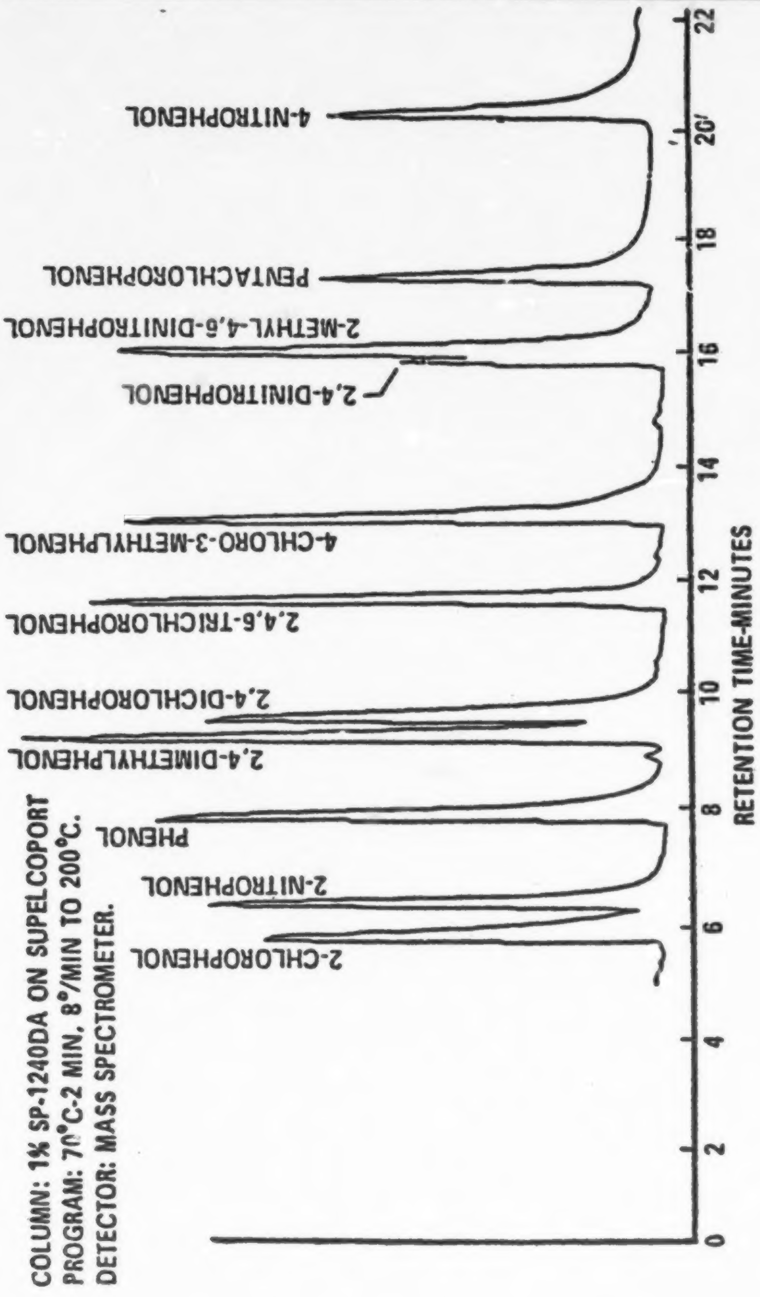


Figure 1. Gas chromatogram of base/neutral fraction



COLUMN: 1% SP-1240DA ON SUPELCOPORT
PROGRAM: 70°C-2 MIN, 8°/MIN TO 200°C.
DETECTOR: MASS SPECTROMETER.

Figure 2. Gas chromatogram of acid fraction

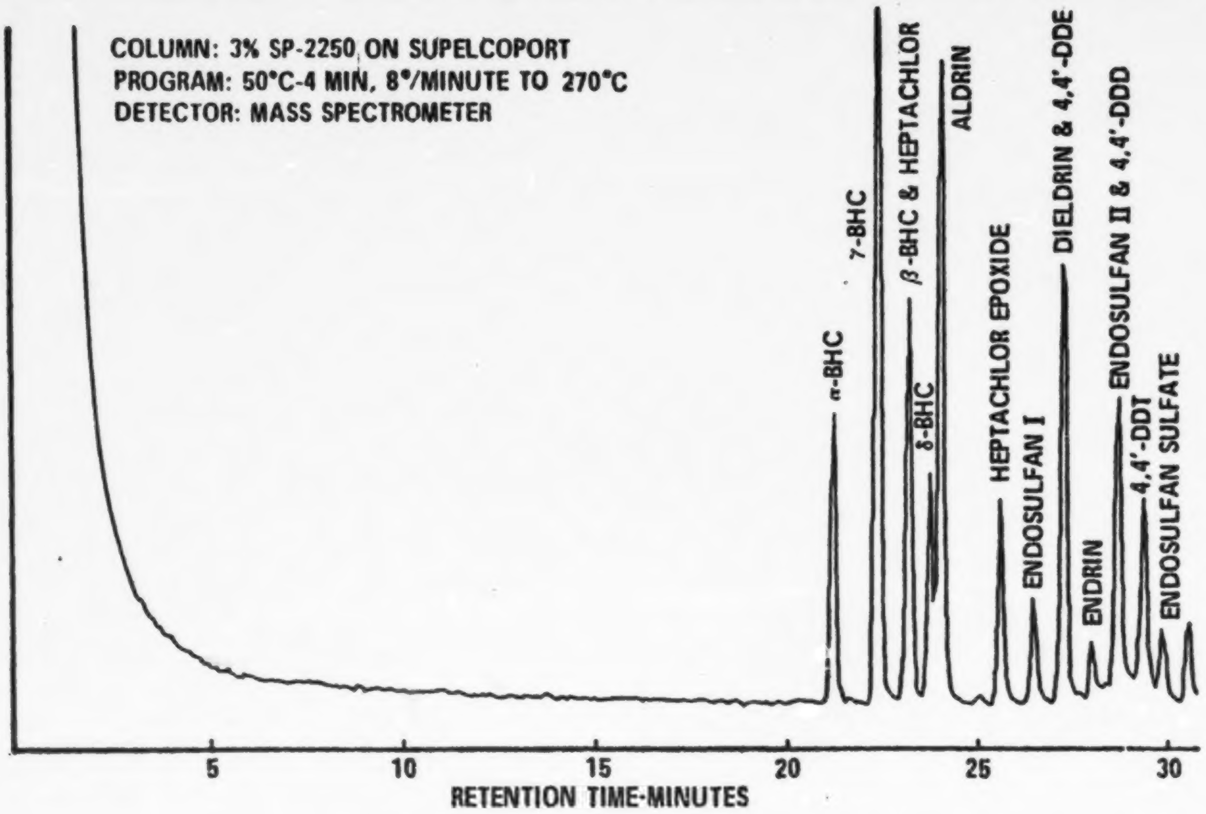


Figure 3. Gas chromatogram of pesticide fraction

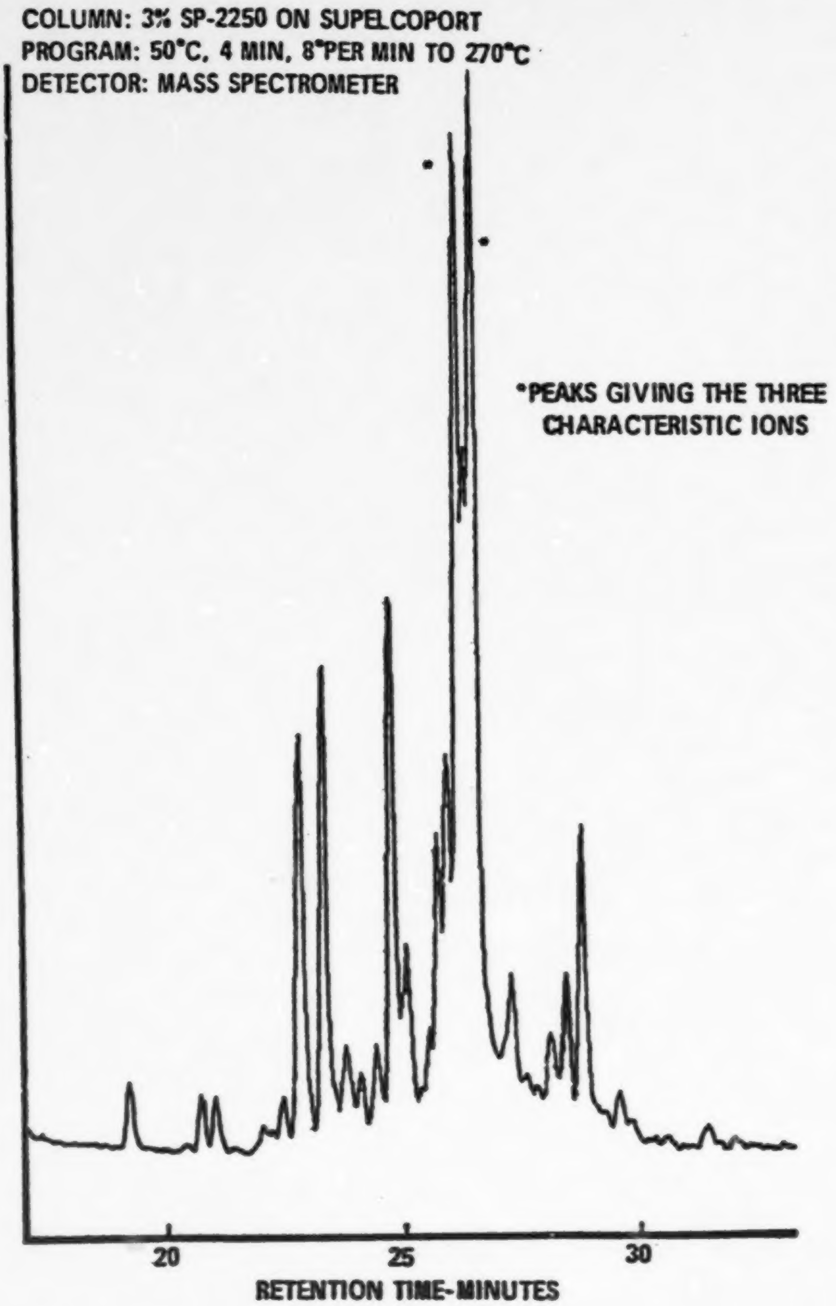


Figure 4. Gas chromatogram of chlordane

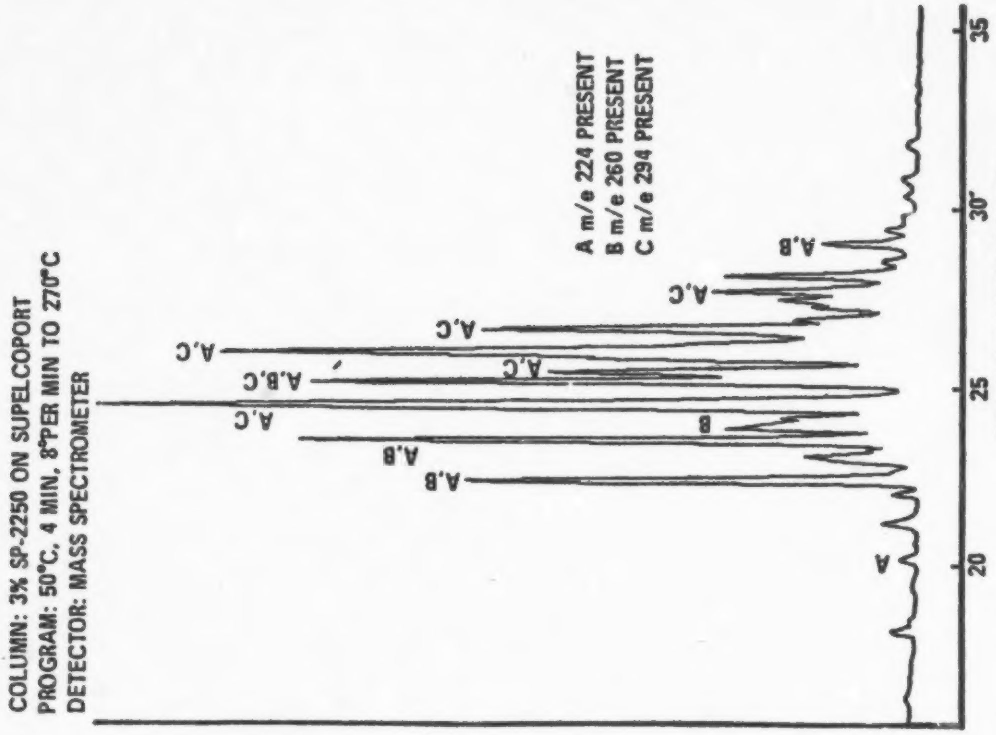


Figure 6. Gas chromatogram of Arochlor 1248

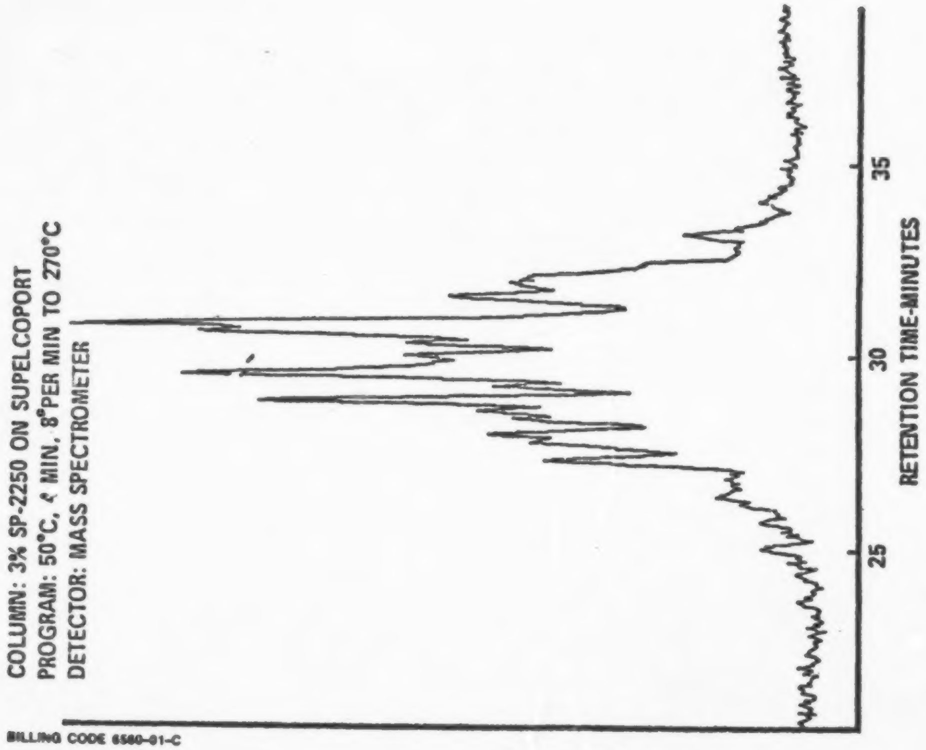


Figure 5. Gas chromatogram of toxaphene

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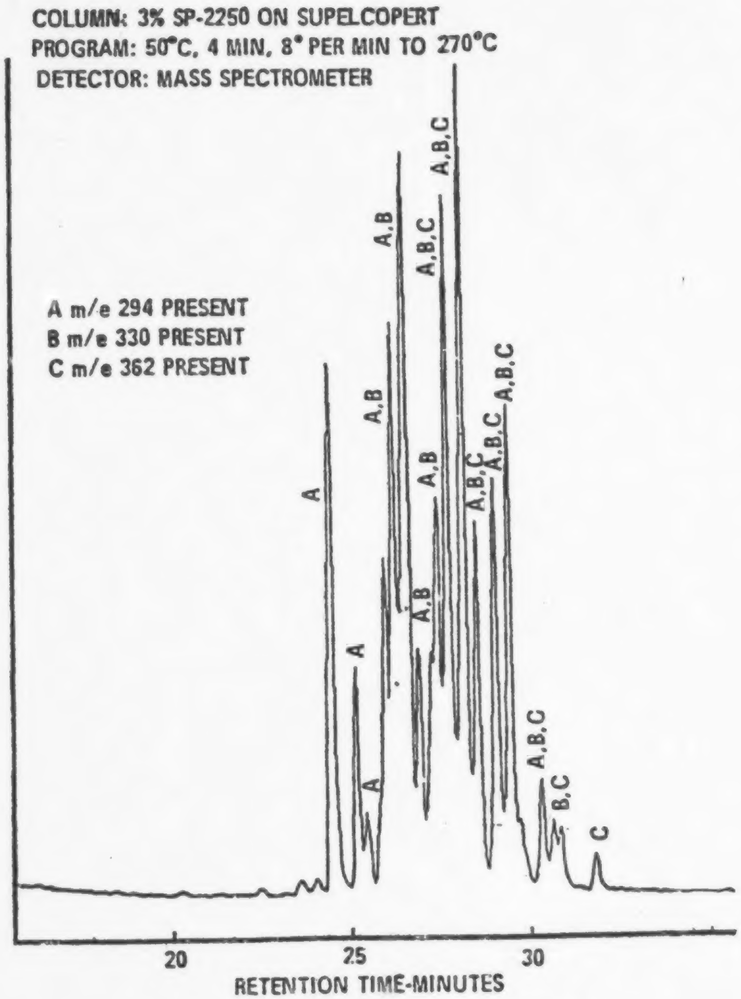
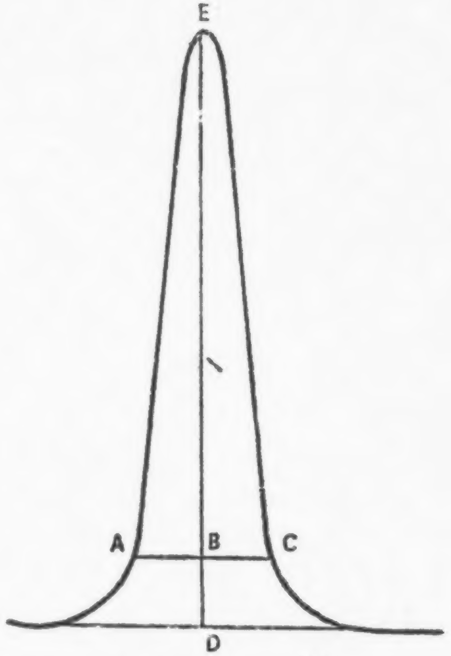


Figure 7. Gas chromatogram of Arochlor 1254

BILLING CODE 6560-01-C



TAILING FACTOR = $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

Figure 1. Tailing factor calculation

REFERENCE MATERIALS FOR DIOXIN ANALYSIS

Analytical Procedures Page 2 of 25

"Tetrachlorodibenzo-p-dioxins in Chemical Wastes, Aqueous Effluents and Soils" by G. F. Van Ness, J. G. Solch, M. L. Taylor and T. O. Tiernan Page 8 of 25

"Sample Preparation and Gas Chromatography-Mass Spectrometry Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin" by R. L. Harless, E. O. Oswald and M. K. Wilkinson Page 19 of 25

- Dioxin standards can be obtained from the sources listed below:

$^{37}Cl_4$-2,3,7,8-TCDD-KOR Isotopes, Cambridge, Mass.
1,2,3,4-TCDD-Analabs, Inc., North Haven, Connecticut
2,3,7,8-TCDD-Dow Chemical Co., Midland, Michigan
1,3,6,8
1,3,7,9
1,4,6,9
1,3,7,8
1,2,6,8
1,2,7,9
1,2,6,9
1,2,7,8
1,2,6,7
1,2,8,9

H. R. Buser
Swiss Federal Research Station
Ch-820
Wadenswil, Switzerland

C. Sample Extraction/Cleanup Procedures

1. Construct a disposable liquid chromatography column as follows. Cut off a Pyrex^R 10 mL disposable pipet at the 4.0 mL mark and use the lower portion of the pipet. Pack the small end with a plug of silanized glass wool. Next add 3 grams of Woelm basic alumina previously activated overnight at 600°C in a muffle furnace and placed in a desiccator for 30 minutes just prior to use.

2. Using a disposable pipet, transfer the sample extract onto the liquid chromatography column.

3. Rinse the centrifuge tube with 2 consecutive 0.3 mL portions of 3% CH_2Cl_2 in hexane, and transfer the rinses to the alumina column.

4. Elute the column with 10 mL of 3% (V/V) Ch_2Cl_2 in hexane and discard the eluent (taking care not to let the column run dry).

5. Elute the column with 20 mL of 20% (V/V) CH_2Cl_2 in hexane and collect the eluent in four 5 mL fractions.

6. Elute the column with 15 mL of 50% (V/V) CH_2Cl_2 in hexane and retain the eluent for analysis.

7. Concentrate the solution to approximately 1 mL, using a stream of prepurified nitrogen as before. Rinse the centrifuge tube wall with an additional 1 mL of CH_2Cl_2 and reconcentrate.

8. Quantitatively transfer the concentrated solution into a 2 mL microreaction vessel with CH_2Cl_2.

Temperature: Injector: 230°C
Column: Initial: 190°C for 2 minutes
Program: 1°C/minute
Final: 230°C and hold until completion of analysis
Transfer Line: 320°C

Conditions for the Mass Spectrometer:

Ionizing Voltage: 70 eV
Static Resolution: 1:12,500 (10 percent Valley)
Source Envelope Pressure: 5 x 10^{-5} torr
Analyzer Pressure: 5 x 10^{-5} torr
Source Temperature: 250°C
Membrane Separator Temperature: 215°C
Transfer Line: 270°C
Masses Monitored: m/z 319.8966, 321.8936, 325.8805, 327.8846

E. Parameters for Gas Chromatographic-Low Resolution Mass Spectrometric (GC-LRMS) Analysis of the extracts:

Instrumentation: Perkin-Elmer Sigma II Gas Chromatograph coupled through a custom-fabricated interface including a single-stage glass jet separator to a Kratos MS-25 Mass Spectrometer equipped with a DS-50SM Data System.

Conditions for the Gas Chromatograph:

Column: 25M WCOT (OV-101) Silica Capillary
Carrier Gas: Hydrogen, 30 lb head pressure
Column Temperature: Programmed from 150°C to 235°C a 5°C/min. Hold at 235°C for 20 min.
Interface Temperature: 250°C
Injector: Split ratio 50:1

Conditions for the Mass Spectrometer:

Selected Ion Monitoring Mode
Ions Monitored: m/z's 319.9, 321.9, 327.9
Ionizing Voltage: 70 eV
Accelerating Voltage: 4 kV

F. Parameters for High Performance Liquid Chromatographic (HPLC) Analysis of the Extracts:

Instrumentation: Varian Model 5021 Microprocessor Controlled High Performance Chromatograph equipped with CDS-111L Data System

2. Capillary Column GC--High Resolution MS Analysis

    a. Correct capillary column GC-HRMS retention time for 2,3,7,8-TCDD.

    b. Correct chlorine isotope ratio for the molecular ion (m/z 320 and m/z 322).

    c. Correct capillary column GC-HRMS multiple ion monitoring responses for TCDD masses and ^{37}Cl-TCDD mass (simultaneous response for elemental composition of m/z 320, m/z 322, and m/z 328).

    d. Correct responses for co-injection of sample fortified with ^{37}Cl-TCDD and TCDD standard.

    e. Response of m/z 320 and m/z 322 (TCDD) must be greater than 2.5 times the noise level.

3. Supplemental criteria which may be applied to samples from highly contaminated sources (high concentrations of TCDD or TCDD in the presence of high concentrations of chlorinated compounds).

    a. COCl loss, indicative of the TCDD structure.

    b. Capillary column GC-HRMS peak-matching analysis of m/z 320 and m/z 322 in real time to confirm the TCDD elemental compositions.

    c. Polar and nonpolar capillary columns to differentiate TCDD isomers.

H. References (Not included in this section)

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Also reported herein are the results of determinations of TCDD in various aqueous effluents, soils and chemical wastes which were collected at a trichlorophenol manufacturing plant. The levels of TCDD in these samples ranged from parts-per-trillion to parts-per-million, and it appears that a significant portion of this is the 2,3,7,8-TCDD isomer.

EXPERIMENTAL

Extraction and Clean-up Methodology. The solvents, petroleum ether, methanol, hexane, methylene chloride, and benzene used in this work were all pesticide quality. Potassium hydroxide, anhydrous sodium sulfate, and sulfuric acid were all reagent grade chemicals. The $^{37}\mathrm{Cl}_4$-2,3,7,8-tetrachlorodibenzo-p-dioxin ($^{37}\mathrm{Cl}_4$-2,3,7,8-TCDD) was purchased from KOR Isotopes, Inc., Cambridge, Massachusetts, USA. The 1,2,3,4-TCDD isomer was purchased from Analabs, Inc., North Haven, Connecticut, USA. The 2,3,7,8-TCDD isomer was obtained from the Dow Chemical Co., Midland, Michigan, USA. Other TCDD isomers utilized in this study were kindly supplied by H. R. Buser, Swiss Federal Research Station, CH-8820, Wädenswil, Switzerland.

Aliquots (typically 1-10g) of air-dried, finely pulverized soil, chemical waste, or aqueous industrial effluents were placed in 125 mL flint glass bottles (Teflon-lined screw caps) and to each sample a quantity of $^{37}\mathrm{Cl}_4$-2,3,7,8-TCDD was added as an internal standard.

Extraction of soil samples was accomplished by adding 40 mL of petroleum ether to the spiked soil sample and shaking for 20 minutes. The organic extract was then quantitatively transferred to a clean 250 mL flint glass bottle, 50 mL of doubly distilled water was added, and the bottle was shaken for 2 minutes. The water layer was removed and the washed organic extract was treated as described below.

Chemical waste samples were extracted by initially adding 10 mL of methanol and 40 mL petroleum ether to the spiked sample contained in a screw-capped 125 mL flint glass bottle. Fifty milliliters of doubly distilled water were then added to the solution, the mixture was agitated for 2 minutes, and the aqueous layer was discarded.

Aliquots of aqueous industrial effluent samples, contained in 125 mL screw-capped bottles, were extracted by adding 40 mL petroleum ether and agitating the mixture for 20 minutes. The aqueous layer was then discarded.

In the case of some finely divided solid samples (for example, rock-soil core samples which were pulverized) it was found that the simple solvent extraction procedures described above were inadequate, since these methods resulted in recovery of little or none of the added $^{37}\mathrm{Cl}_4$-2,3,7,8-TCDD internal standard. For such samples it was necessary to employ a lengthy Soxhlet extraction procedure, using pure methylene chloride as the solvent. Extraction periods up to three days in duration were required for some samples of this type in order to achieve acceptable recoveries of the $^{37}\mathrm{Cl}_4$-2,3,7,8-TCDD spike.

The organic extracts from soil, chemical waste, or aqueous industrial effluents, obtained as described above, were subsequently subjected to identical clean-up procedures, which entailed: 1) washing the organic layer with 50 mL of 20% potassium hydroxide, by agitating for 10 minutes, followed by removing and discarding the basic layer; 2) washing the organic layer with 50 mL doubly distilled water, by shaking for 2 minutes, and discarding the aqueous layer;

3) cautiously adding 50 mL of concentrated sulfuric acid, and shaking for 10 minutes; then, allowing the mixture to stand for an additional 10 minutes, and discarding the acid layer (repeating this acid washing until no color was visible in the acid layer); 4) adding to the organic layer 50 mL of doubly distilled water and shaking for 2 minutes, then discarding the aqueous layer; and finally, 5) drying the organic layer over 10g of anhydrous sodium sulfate.

Each dried organic extract was concentrated to near dryness in a glass test tube and then transferred to an alumina micro-column. The micro-column was made by cutting off the top section of a 10 mL disposable Pyrex pipet at the 4.0 mL mark and using the lower portion as the column. A plug of silanized glass wool was inserted into the tip of the pipet followed by 2.8 g of Woelm basic alumina, previously activated at 600°C overnight and cooled in a desiccator just prior to use. The micro-column was eluted first with 10 mL of 3% methylene chloride-in-hexane, then with 15 mL of 20% methylene chloride-in-hexane and these effluents were discarded. Next, the column was eluted with 15 mL of 50% methylene chloride-in-hexane, and this entire column effluent was retained and concentrated to a volume of 0.3-0.5 mL in a stream of dry nitrogen. The concentrated residue was transferred (using methylene chloride to rinse the container) to a silanized Reacti-Vial (Pierce Chemical Co.). The solution in the Reacti-Vial was then evaporated just to dryness, in a stream of nitrogen, the vial was tightly capped and stored at +5°C. Just prior to analysis the residue from each sample was reconstituted by addition of benzene.

It should be noted that the elution chromatography procedures just described must be applied with some caution. In developing these methods, it was found that the TCDD elution characteristics of the alumina column varied markedly depending upon the sample matrix. Apparently, each type of sample conditions/deactivates the column somewhat differently, depending upon the sample constituents. It is important therefore, to determine the elution characteristics for each type of sample by preliminary screening, using $^{37}Cl_4$-2,3,7,8-TCDD as an indicator of recovery.

In addition to the elution chromatography clean-up, some samples which contained particularly large quantities of organic compounds which interfere with the TCDD determination were subjected to High Performance Liquid Chromatography (HPLC). The HPLC instrument used is a Varian Model LC-5021 equipped with a UV detector (235 nm). A Dupont Zorbax ODS column (25 cm x 6.2 mm) was used, and the column was operated at a temperature of 50°C, in the isocratic mode, with 100% methanol as the solvent. The starting pressure was 952 psig and the flow rate was 2.5 ml/min. The procedures employed are similar to those described by Nestrick et al (12).

GC-MS Instrumentation and Procedures. Gas chromatographic-high resolution mass spectrometric (GC-HRMS) analyses for this study were accomplished using an instrument which consists of a Varian 3740 Gas Chromatograph coupled through an AEI silicone membrane separator to an AEI Double-Focusing, Double-Beam MS-30 Mass Spectrometer. The mass spectrometer is equipped with a unique electrostatic analyzer (ESA) step-scan circuit developed by this laboratory (13-15). This circuit permits as many as 4 mass peaks to be monitored, essentially simultaneously, by alternately stepping and scanning the ESA voltage, so that four distinct, narrow portions of the mass scale (each typically 0.07 AMU wide) are sequentially scanned. Data acquisition and control of the step-scan sequence is accomplished using a Nicolet 1074 Signal Averaging Computer. With this GC-HRMS instrument, 10 picogram/injection sensitivity is routinely achieved for TCDD with a signal/noise ratio of 10:1, at a static resolution of 1:12,500.

Specific operating conditions for the GC-HRMS are as follows. The gas chromatographic column is a 1.8 m x 2 mm I.D. coiled glass column packed with 3% Dexsil 300 on Supelcoport (100/120 mesh). The carrier gas is helium at a flow rate of 30 mL/min. The column was operated isothermally at a temperature of 240°C, while the injector was maintained at 250°C and the transfer line at 285°C. The AEI MS-30 Mass Spectrometer was operated with a static resolution of 1:12,500 (10% valley) and an ionizing voltage of 70eV. The ions normally monitored are m/e 319.8966, 321.8936, 325.8805, and 327.8846. The first two masses are major peaks in the mass spectrum of 2,3,7,8-TCDD, the third is a prominent ion in the spectrum of PCBs, and the last is characteristic of the $^{37}Cl_4$-2,3,7,8-TCDD standard. For these analyses, the membrane separator was maintained at a temperature of 215°C, while the ion source temperature was 250°C.

Calibration Procedure. As indicated above, $^{37}Cl_4$-2,3,7,8-TCDD was utilized throughout this work as an internal standard. A calibration curve was prepared by analyzing a series of standard solutions containing varying concentrations of 2,3,7,8-TCDD, each containing the same concentration of $^{37}Cl_4$-2,3,7,8-TCDD, and plotting the ratio of the areas of the peaks which are indicative of 2,3,7,8-TCDD and $^{37}Cl_4$-2,3,7,8-TCDD as a function of the concentration of 2,3,7,8-TCDD. Use of the internal standard technique automatically corrects the results for any losses of TCDD incurred during sample processing. Simultaneous monitoring of the two masses indicative of 2,3,7,8-TCDD, as well as the mass corresponding to the $^{37}Cl_4$-2,3,7,8-TCDD internal standard, actually provides two analytical determinations at the same time. That is, 2,3,7,8-TCDD can be quantitated on the basis of both the signal at m/e 319.8966 and that at m/e 321.8936. The theoretically expected ratio of these two isotopic peaks of 2,3,7,8-TCDD is $\frac{I_{319.8966}}{I_{321.8936}} = 0.77$. In practice, the ratio of the signals obtained for these two masses is affected by the presence of ions from interfering substances having mass to charge ratios which are nearly identical to those from TCDD. Also, at low concentrations, the number of ions being detected is quite small, and the ratio of the two masses is influenced by ion statistics. Based upon our experience in the analysis of more than 500 standard and spiked blank samples containing TCDD the m/e 319.8966:m/e 321.8936 ratio has been observed to vary between 0.35 and 1.35. Thus samples yielding analytical data which exhibit ratios falling within this range are considered to be acceptable, while samples yielding ratios outside this range are presumed to contain interferences, and are consequently reprocessed.

As noted above, a fourth mass (m/e 325.8805) is routinely monitored to obtain an indication of the presence of polychlorinated biphenyls (PCBs) which can interfere with quantitation of TCDD. If present in the sample in very large quantities, some PCBs can survive the extensive clean-up and preseparation procedures and remain in the sample which enters the mass spectrometer ion source.

In the present studies, samples were typically spiked with 10 ng of $^{37}Cl_4$-2,3,7,8-TCDD. However, in some cases, as much as 50 ng of the internal standard was added, where relatively large concentrations of native TCDD were present in the sample. Although all the calibration and spiking procedures were accomplished by using the 2,3,7,8-TCDD isomer, it should be noted that the GC-HRMS method described above is not isomer specific, and actually detects 2,3,7,8-TCDD and several of the other 21 TCDD isomers which may be present in the sample. The lower trace in Figure 1 illustrates the 4-peak array obtained for a mixture of 50 picograms of 2,3,7,8-TCDD and 1.0 ng of $^{37}Cl_4$-2,3,7,8-TCDD, while the 4-peak array resulting from injection of a portion of the extract of an aqueous industrial effluent sample is shown in the upper trace in Figure 1.

RESULTS AND DISCUSSION

Table 1 presents the results of analyses of several spiked water samples for TCDD. These water samples were prepared by a United States Environmental Protection Agency (EPA) laboratory, and were included as unidentified quality control samples in a set of 12 industrially-related water samples shipped to Wright State for analysis. The average concentrations of TCDD determined by our laboratory are seen to be in reasonably good agreement with the concentrations added to the sample by EPA. The negative result obtained for the blank water sample indicates that cross contamination of samples has not occurred. Overall, these data show that the methodology is quite satisfactory.

Analytical results for a series of aqueous industrial effluent samples are listed in Table 2. These were essentially unfiltered water samples which contained small amounts (< 0.01g/10 mL) of sediment. Samples were shaken to resuspend the sediment before aliquots were withdrawn for analysis. Of 20 samples of this type analyzed, 5 were found to contain TCDD. Concentrations of TCDD in these samples ranged from zero (none detected at a minimum detectable concentration of 10 pg/g) to 100 pg/g. The average recovery of the $^{37}Cl_4$-2,3,7,8-TCDD internal standard for this set of samples was 78%.

Typical results obtained from analyses of soil samples collected at an industrial site (a trichlorophenol manufacturing plant) are shown in Table 3. About eightyfive percent of the soil samples examined were found to contain TCDD, and a broad range of TCDD concentrations were observed in these samples (< 20 pg/g to 0.6 μg/g). Excellent recoveries of the $^{37}Cl_4$-2,3,7,8-TCDD internal standard added to these samples were realized, as can be seen in Table 3. No quality control samples containing native TCDD were provided by the EPA in this set of samples.

Industrial chemical and sludge samples from a trichlorophenol manufacturing plant presented the most difficulty in preparation and analysis. Residues from chemical retorting of chlorinated phenols which were analyzed were generally found to be homogeneous and amenable to the procedures described above. Other industrial sludge samples, however, were found to be very complex, and preparation of these samples proved to be quite tedious. Several of

Figure 1. GC - HRMS Four-Peak Array Obtained for a Sample Extract (7) and a 2,3,7,8 TCDD Standard by Rapidly Step-Scanning the Mass Spectrometer As 2,3,7,8 TCDD Elutes from the GC Column

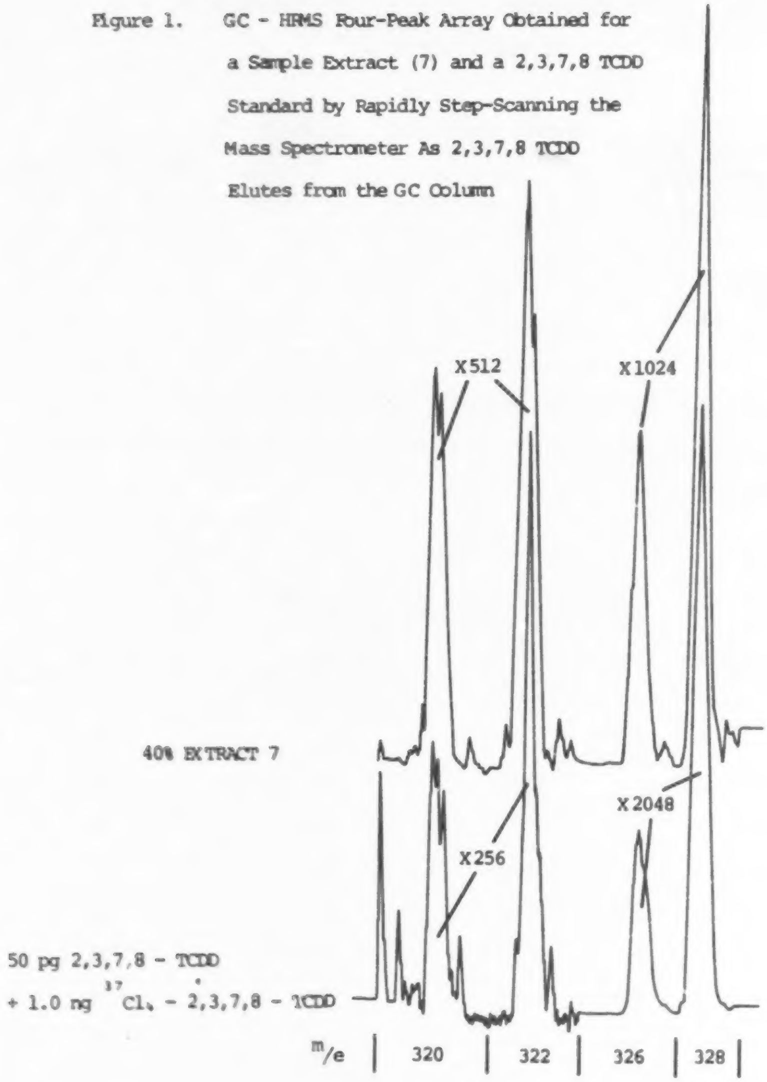

Table 1

Results of Determination of TCDD in Water Samples Spiked by an EPA Laboratory[a].

Sample No.	Quantity of TCDD Added (pg/g)	Average Quantity of TCDD Found[b,c] (pg/g)	Minimum Detectable Concentration (pg/g)	% Recovery $^{37}Cl_4$-2,3,7,8-TCDD
2	25	25	10	83
3	50	51	10	79
8	10	19	10	118
12(Blank)	0	N.D.	10	115

[a] Samples spiked by EPA Toxicant Analysis Center, Gulfport, Miss.

[b] Average of concentrations determined on basis of m/e 320 and m/e 322 signals.

[c] N.D. = None detected.

Table 2

Results of Determination of TCDD in Aqueous Industrial Effluent Samples

Sample No.	Quantity of TCDD Found (pg/g)[a]. m/e 320	m/e 322	Average	Detectable Concentration (pg/g)	% Recovery $^{37}Cl_4$-2,3,7,8-TCDD
1	12	22	17	10	82
4	N.D.	N.D.	N.D.	15	76
5	N.D.	N.D.	N.D.	15	85
6	N.D.	N.D.	N.D.	30	50
7	91	109	100	25	58
9	N.D.	N.D.	N.D.	10	98
10	N.D.	N.D.	N.D.	10	92
11	N.D.	N.D.	N.D.	20	82

[a] N.D. = None Detected.

Table 3

Results of Determination of TCDD in Soil Samples from an Industrial Site

Sample No.	Quantity of TCDD Found (ng/g)[a] m/e 320	m/e 322	Average	Minimum Detectable Concentration (pg/g)	% Recovery $^{37}Cl_4$-2,3,7,8-TCDD
9	0.97	1.22	1.09	50	106
11	20.3	24.4	22.4	300	98
13	N.D.	N.D.	N.D.	20	104
19	538	579	559	2300	108
23	3.30	3.54	3.42	250	81

[a] N.D. = None Detected

Table 4

Results of Determination of TCDD in Industrial Chemical and Sludge Samples

Sample No.[c]	Sample Description	Quantity of TCDD Found[a] m/e 320	m/e 322	Average	Minimum Detectable Concentration	% Recovery $^{37}Cl_4$-2,3,7,8-TCDD
14	TCP Process-Still Bottom[b]	109μg/g	113μg/g	111μg/g	0.11μg/g	82
15U	Sump Fluid	54pg/g	71pg/g	63pg/g	20pg/g	88
15L	Sump Fluid	637ng/g	714ng/g	676ng/g	30ng/g	79
16U	Sludge-Liquid	407ng/g	482ng/g	445ng/g	14ng/g	83
16L	Sludge-Solid	377ng/g	370ng/g	374ng/g	2ng/g	99
32	Hexachlorophene Clay Filter	N.D.	N.D.	N.D.	70pg/g	98
36	TCP Process-Sludge[b]	90pg/g	67pg/g	79pg/g	50pg/g	40
38	TCP Process Discharge[b]	21ng/g	22ng/g	22ng/g	0.5ng/g	69
312	Wood Preserving Retort Sludge	N.D.	N.D.	N.D.	140pg/g	78

[a] N.D. = None Detected
[b] TCP = trichlorophenol
[c] U = upper layer of two distinct layers
L = lower layer of two distinct layers

the sludge samples contained two distinct layers which were analyzed separately. Table 4 lists the results obtained from the analyses of nine different samples of these types. The average recovery of the internal standard added to these samples was 80%, again quite acceptable. The levels of TCDD concentrations in these samples ranged from pg/g to µg/g.

Isomer Specific Analyses: Preliminary Results. The GC-HRMS technique described above is a highly specific method for quantitating tetrachlorodibenzo-p-dioxins present in complex samples. The GC-HRMS technique is not, however, necessarily isomer specific; that is, TCDD isomers in addition to 2,3,7,8-TCDD may, depending upon their chromatographic and mass spectrometric properties, be detected and identified as 2,3,7,8-TCDD. However, it is of interest to determine which of the 22 possible TCDD isomers are present in the sample, since this information is useful in determining the origin of the tetrachlorodibenzo-p-dioxin contamination, and the relative toxicity of the sample. For these reasons we have recently established the capability to perform isomer-specific TCDD analyses.

A Varian 3740 Gas Chromatograph coupled directly to an Extranuclear Quadrupole Mass Spectrometer was employed for the determination of the distribution of isomers in sample extracts previously analyzed by GC-HRMS. Conditions for the high resolution GC-low resolution mass spectrometric analysis of TCDD isomers are as follows. The chromatographic column utilized is a 60-meter OV-101 capillary (WCOT) column (Supelco, Inc.), and hydrogen is used as the carrier gas at a flow rate of 40 cm/sec. The column is operated isothermally at 190°C for 2 min. following injection of the sample, and the temperature is then increased at a rate of 1°C/min. to a final temperature of 230°C. The injector was maintained at a temperature of 300°C and the transfer line at 320°C. Splitless injection was utilized for these analyses.

The mass spectrometer was operated at a resolution of 1:300, with the ionizing voltage at 20 eV and the ion source temperature at 150°C. Both m/e 320 and m/e 322 can be monitored by using the peak switching capability of this instrument. The analyzer region temperature was maintained at 110°C and the transfer line at 350°C for these determinations. Figure 2 shows three mass chromatograms (obtained by monitoring m/e 322) for samples containing TCDD. The mass chromatogram at the top was obtained for a mixture of TCDD isomer standards and shows the separation of the twelve TCDD isomers which are identified on the figure. The mass chromatograms at the center and at the bottom of the figure were obtained for extracts of a soil sample and an industrial sludge sample, respectively. These results indicate that the majority of the TCDD present in these samples is quite likely the 2,3,7,8-TCDD isomer. However, availability of all of the 22 isomers of TCDD is obviously a prerequisite for unequivocal quantitative determination of each of these isomers which may be present in such samples. The ten remaining TCDD isomers are currently being synthesized in our laboratory, and work in this area is continuing.

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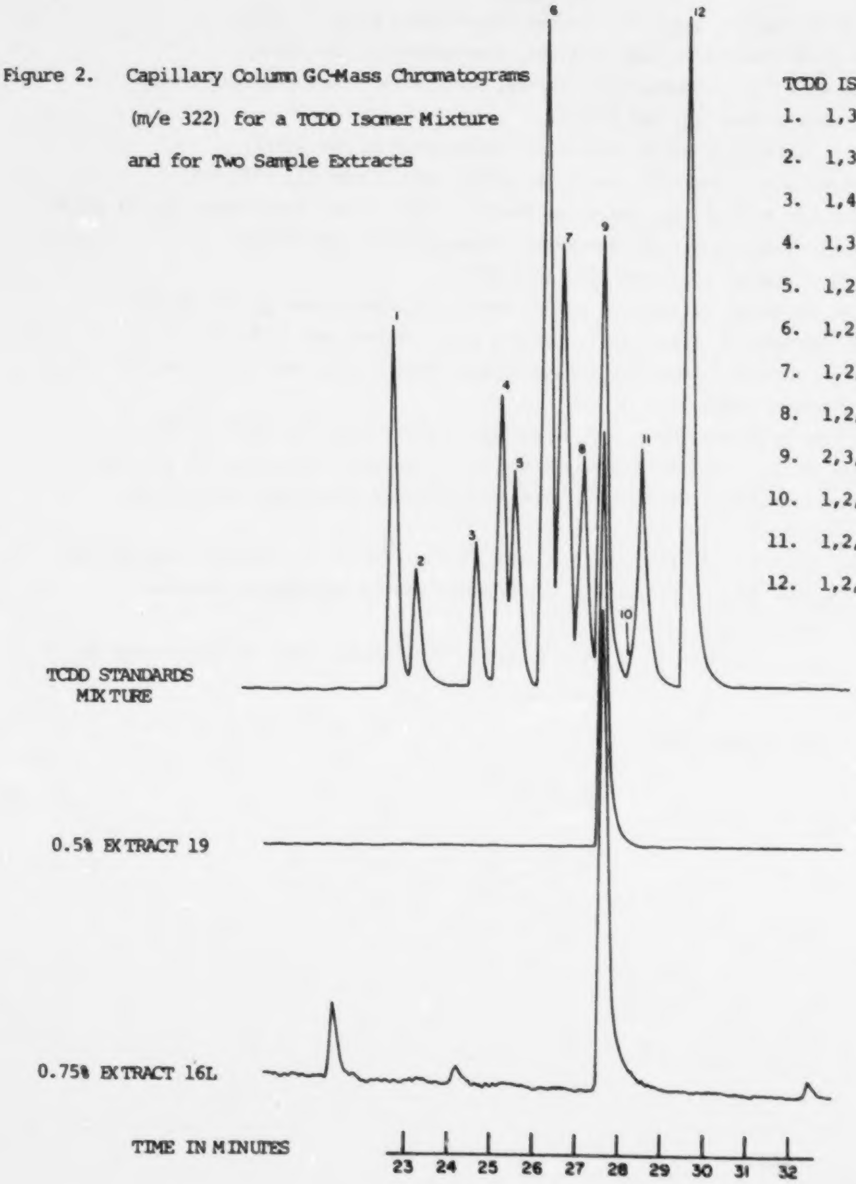
Figure 2. Capillary Column GC-Mass Chromatograms (m/e 322) for a TCDD Isomer Mixture and for Two Sample Extracts



	TCDD ISOMERS
1.	1,3,6,8
2.	1,3,7,9
3.	1,4,6,9
4.	1,3,7,8
5.	1,2,6,8
6.	1,2,7,9
7.	1,2,6,9
8.	1,2,3,4
9.	2,3,7,8
10.	1,2,7,8
11.	1,2,6,7
12.	1,2,8,9

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Sample Preparation and Gas Chromatography–Mass Spectrometry Determination of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin

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Analytical extraction, clean-up procedures, and capillary column gas chromatography–high resolution mass spectrometry methods are presented for determination of low concentrations (pg/g levels) of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The application of these procedures and methods in the analysis of human milk, beef liver, fish, water, and sediment is described. The TCDD methodology provided a mean % recovery of 80% for 2.5 to 10 ng $^{37}Cl_4$-TCDD, internal standard, and a mean % accuracy of ±23% for 1 to 1250 pg TCDD in quality assurance samples. The precision of the GC-HRMS technique was determined to be ±20% relative to 2 to 10 pg TCDD quantification standards during daily operations.

The highly toxic compound, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), may be formed as a by-product in manufacturing processes utilizing tetrachlorobenzene to produce trichlorophenol. Under high pressure, high temperature, and very basic conditions 1,2,4,5-tetrachlorobenzene is hydrolyzed to the 2,4,5-trichlorophenate. The chlorinated phenol is produced upon acidification. Unfortunately, a condensation can take place in this reaction which results in the formation of TCDD. Herbicides containing esters of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) manufactured from trichlorophenol have been found to contain trace amounts of TCDD. Recent reports have indicated chlorinated dibenzo-*p*-dioxins including TCDD may be formed in combustion processes. TCDD has been recognized as an extremely toxic (LD_{50} 0.6 μg/kg, female guinea pig, most sensitive species) (*1*), carcinogenic (*2*), and teratogenic (*3*) compound.

Because of its toxicity and occurrence as a trace contaminant in chemical products, it is necessary to analyze for TCDD at the low parts per trillion (ppt) concentration range, which is below the usual limits of detection for pesticide residue analysis. Methods for determining ppt TCDD in sample extracts using high resolution mass spectrometry (HRMS) (*4*, *5*), packed column gas chromatography (GC) in conjunction with low and high resolution MS (*6–8*), high resolution gas chromatography with low resolution MS (*9*), and GC-negative ion chemical ionization MS (*10*) have been reported.

The analysis of human, biological, and environmental samples for TCDD contamination in the ppt concentration range is complicated by the presence of many interfering components ranging from naturally occurring compounds to industrial pollutants. Therefore, an extremely efficient and specific analytical clean-up procedure is a prerequisite for ppt TCDD analysis utilizing GC-MS detection techniques. The GC-MS detection technique must be ultra-sensitive and highly specific because of the required low ppt detection limits. High resolution glass capillary column GC interfaced with medium and high resolution MS specific mass detection provides the required GC resolution of components, MS sensitivity, and specificity for TCDD analysis in the 0.03 to 100 ppt concentration range.

This paper will describe the current sample preparation procedures and capillary column GC/HRMS techniques developed and applied by EPA laboratories for the isolation and quantitative determination of TCDD residues in human, biological, and environmental samples. TCDD results generated in the EPA laboratory and collaborating laboratories, are evaluated and released by designated EPA officials. Therefore, only the results of quality assurance samples and samples with unusual contamination are discussed in this paper.

EXPERIMENTAL

Safety. TCDD is toxic and can pose grave health hazards if handled improperly. Techniques used for handling radioactive and infectious materials are applicable to TCDD. Only qualified individuals who are trained in laboratory procedures and are familiar with the hazards of TCDD should handle this substance. Females of childbearing age should not work with this material.

A good laboratory practice involves routine physical examinations and blood checks of employees working with TCDD. Also facial photographs using oblique photoflood lighting should be periodically taken to detect chloracne, which is an early indication of TCDD exposure.

Instrumentation. A Varian Model 2700 GC interfaced with a Varian 311A MS was utilized for these analyses. The interface design (*11*) ensured maximum transfer efficiency. The GC was equipped with a 30 m × 0.25 mm i.d. SE-30 WCOT glass capillary column. The MS was equipped with a turbo-molecular vacuum pumping system. combination chemical ionization (CI) electron impact (EI) ion source (operated in the EI mode), and a Varian eight-channel hardware (manual control) Multiple Ion Selection (MIS) device. The vacuum system easily accommodated the 5 mL/min helium flow from the GC/MS interface and did not contribute detectable background contamination. The MIS device was operated in the normal coupled electric mode (jumping the acceleration voltage). Each MIS channel was equipped with individual controls for selecting a specific acceleration voltage, measuring range, out-put signal bandwidth, compensation for background contamination, and integration rate. The intensities of the selected masses were monitored in a time-division multiplex system, setting alternatively to each of the selected masses and recording their intensities simultaneously on an eight-channel Soltec recorder. The adjustable integration rate, 0.01 to 1 s was sufficient to accurately reproduce capillary column peaks 2 s wide at half height.

Capillary Column GC/HRMS Multiple Ion Selection Analysis. The magnet current was tuned to perfluorokerosene (PFK; *m/z* 318.9793 and the MS was adjusted for 5000 to 9000 mass resolution. The ESA voltage was monitored and used in calculating the exact acceleration voltage required for the masses, *m/z* 327.8847 $C_{12}H_4O_2{}^{37}Cl_4$, *m/z* 321.8936 $C_{12}H_4O_2{}^{35}Cl_3{}^{37}Cl$, and *m/z* 319.8965 $C_{12}H_4O_2{}^{35}Cl_4$. The calculated values were introduced to MIS channels 2, 3, and 4. Two microliters of quantification standard, 500 pg/μL ^{37}Cl-TCDD (labeled 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, ^{37}Cl-TCDD isotopic purity greater than 98%) and 1 pg/μL TCDD, and 0.5 μL of *n*-tetradecane (keeper, improves chromatographic resolution) were injected into the capillary column (on column splitless injection). The GC parameters were: column temperature 80 °C; 6 min isothermal then programmed at 34 °C/min to 265 °C; solvent vent closed at 14 min; MIS analysis initiated at 16 min; TCDD retention time 23 ± 0.25 min. Other GC-HRMS parameters were: injection port 260 °C; GC transfer line 255 °C; ion source 240 °C; specific and variable acceleration voltage, 3 kV maximum; electron energy 70 eV; filament emission 1 mA; mass resolution 5000 to 10 000; multiplier gain greater than 10^6.

COCl Loss Analysis. The magnet current was tuned to PFK *m/z* 254.9856 and the exact acceleration voltages required for TCDD masses *m/z* 256.9327, *m/z* 258.9298, *m/z* 319.8965, *m/z* 321.8936, and the *m/z* 327.8847 corresponding to ^{37}Cl-TCDD, were introduced into respective MIS channels. The analysis was performed adhering to the previously described time schedule of events. The GC-HRMS MIS five-channel simultaneous responses for ^{37}Cl-TCDD and TCDD were observed and recorded at the correct GC retention time for TCDD.

Elemental Composition Analysis. The MS was adjusted for 10 000 mass resolution utilizing PFK *m/z* 318.9793 as reference. The capillary column GC-HRMS peak matching analysis was initiated adhering to the exact time schedule of events utilized in the GC-HRMS MIS analyses. The reference mass and the exact mass range of interest were displayed alternately and were visible simultaneously on the MS oscilloscope.

Precision and Accuracy of GC-HRMS Techniques. The precision and accuracy of capillary column GC-HRMS analyses were dependent on: (1) stability of MS electronic circuits; (2) sample preparation procedure (specificity and efficiency); (3) precise dilution or concentration of 60-μL sample extracts; (4) precise injection volumes; (5) capillary column resolution of components.

The MS, when adjusted for ca. 7500 mass resolution and used as a GC detector in GC-HRMS MIS analysis, provided positive responses for those components which eluted from the GC and produced a molecular ion or fragment ion within ±30 millimass units of TCDD masses *m/z* 319.8965, *m/z* 321.8936, and ^{37}Cl-TCDD mass, *m/z* 327.8847. The intensity of the MIS response for a component other than TCDD was dependent on the difference in exact masses (i.e., only a fraction of the total intensity of a component mass differing from TCDD by ±30 millimass was detected in MIS analysis). Therefore, interference from contamination, chlorinated compounds, hydrocarbons, etc., was minimized or not detected. The MIS responses for ^{37}Cl-TCDD and TCDD were reproducible and linear relative to the amount injected. Two TCDD concentration ranges, 0.2 to 2 pg and 2 to 10 pg, were utilized to provide the most efficient and accurate quantification of TCDD residues. Sample extracts (60 μL) were concentrated or diluted as required for quantification purposes. The reproducibility of peak height responses during daily operation was observed to be ±20% relative to 1 pg/μL or 5 pg/μL TCDD quantification standards. The TCDD *m/z* 320 and *m/z* 322 chlorine isotope ranged from 0.75:1 to 0.98:1. The variation from the theoretical chlorine ratio, (0.76:1), was attributed to MIS integration rate, narrow bandwidth of capillary column peaks, and the small amount of TCDD analyzed in the presence of minor amounts of contamination.

Because of the widespread distribution of PCBs, the accuracy of ^{37}Cl-TCDD determination primarily depends on the sample preparation efficiency and specificity, and the capillary column GC resolution of components. The MS mass resolution, ca. 45 000, required to separate ^{37}Cl-TCDD *m/z* 327.8847 and PCB *m/z* 327.8775 is not feasible owing to MS limitations. For occasional and highly contaminated sample extracts, the ^{37}Cl-TCDD *m/z* 328 peak height was determined utilizing the PCB *m/z* 326 peak height to calculate the PCB contribution to the *m/z* 328, a mixture of ^{37}Cl-TCDD and PCB.

The GC/HRMS peak matching accuracy for known elemental compositions was determined to be ±2 millimass units at 9500 mass resolution with PFK as reference. The PFK reference mass, *m/z* 318.9793, and TCDD mass were observed to be exactly superimposed on the MS oscilloscope in real time at the exact GC-HRMS retention time of TCDD. The TCDD isomers were also confirmed in these analyses.

The equation shown below was used to calculate the mean % accuracy for QA samples.

$$\%\ \text{Accuracy} = \pm[|x_i - \bar{x}|/\bar{x}]\ (100)\ \text{(per individual analysis)}$$

$$\text{Mean \% Accuracy} = \pm \frac{\sum_{i=1}^{n} [|x_i - \bar{x}|/\bar{x}\,(100)]_i}{n}$$

(for all analysis performed)

Accuracy = the difference between an individual value x_i (where x_i = TCDD detected) and the true or correct value of the quantity measured $\bar{x}$ (where $\bar{x}$ = TCDD fortification level)

Quality Assurance (QA) Program. The sample preparation laboratory assigned identification numbers to all samples. The samples and QA samples were fortified with 2.5 to 10 ng of ^{37}Cl-TCDD prior to analytical extraction and cleanup. The QA samples were also fortified with 0 to 1250 pg of TCDD. A method blank was included as part of the QA sample package. The sample extracts and quantification standards, ^{37}Cl-TCDD and TCDD, were submitted to the GC-MS laboratory in a blind fashion (i.e. there was no way to distinguish between QA and actual samples). The efficiency, accuracy, precision, and validity of ppt TCDD analyses are dependent upon the incorporated quality assurance program.

Analytical Extraction and Clean-Up Procedures. *Reagents.* The hexane, acetone, benzene, methylene chloride, and acetonitrile were Mallinckrodt nanograde. The carbon tetrachloride was Fisher ACS grade (water, 0.01% maximum) and the ethyl alcohol was Matheson Coleman and Bell, pesticide quality. The alumina was Woelm neutral activity grade I. The Florisil, Floridin Co., was from a lot suitable for pesticide residue work. The sodium carbonate, sodium sulfate, potassium hydroxide, and sulfuric acid were Mallinckrodt AR grade. The sodium carbonate, and sodium sulfate were Soxhlet-extracted overnight with methylene chloride and dried at 200 °C. The water was passed through a column of activated carbon and distilled. The nitrogen used for solvent evaporation was Zero Grade obtained from Liquid Air, Inc., New Orleans, La. All solvents and chemicals were checked to verify the absence of background contamination.

The labeled 2,3,7,8-tetrachlorodibenzo-*p*-dioxin having an isotopic purity greater than 98% ^{37}Cl$_4$ was obtained from Eco-Control, Inc. (71 Rogers Street, Cambridge, Mass. 02142). Analytical standards of 2,3,7,8-TCDD were obtained from Dow Chemical Co. (Midland, Mich.), IIT Research Institute (3441 So. Federal Street, Chicago, Ill. 60616), and Eco-Control, Inc.

Preparation of Chromatographic Columns. Alumina chromatographic columns were prepared by packing 4.5 cm of neutral alumina into a clean and dry $5^3/_4$-inch (0.5-cm i.d.) disposable Pasteur pipet. The alumina was topped with 0.5 cm of anhydrous granular Na_2SO_4. The column was washed with 4 mL of methylene chloride and residual solvent was forced from it using a stream of dry nitrogen. The columns were stored in an oven at 225 °C (minimum of 24 h) and were equilibrated to room temperature prior to use by placement in a desiccator over Drierite.

Florisil chromatographic columns (11 × 500 mm) were packed with 15 g of 60–120 mesh Florisil (activated at 225 °C for 24 h). The column was topped with 2.5 cm of anhydrous granular sodium sulfate and pre-washed with 100 mL of hexane.

Sample Preparation Using Acid/Base Procedure. *Fish and Lean Tissue.* Tissue samples were ground to obtain a homogeneous sample. A 10 to 20 g sample was weighed into a 100-mL boiling flask. Five to 10 ng of ^{37}Cl-TCDD standard solution, 20 mL of ethyl alcohol, and 40 mL of 45% potassium hydroxide solution were added. The flask was heated under reflux with stirring for 2.5 h. After cooling, the solution was quantitatively transferred to a separatory funnel and the flask was rinsed with 10 mL of ethyl alcohol followed by 20 mL of hexane. The solution was extracted with four 25-mL portions of hexane and the hexane extracts were combined.

Adipose Tissue. The samples were ground or rendered if necessary to obtain a representative sample that was free from connective and other tissue. Ten to 20 g of tissue were fortified with 5 to 10 ng ^{37}Cl-TCDD and 15 mL of distilled water was added. The mixture was refluxed with aqueous KOH/ethanol and extracted as described in the lean tissue procedure.

Milk. Two and one-half ng of ^{37}Cl-TCDD standard solution were added to 10 to 20 g of milk. The sample was refluxed with aqueous KOH/ethanol and extracted as described in the lean tissue procedure.

Water. One kg of a well shaken water sample (including particulate matter, if present) was fortified with 2.5 ng ^{37}Cl-TCDD standard solution and extracted with three 100-mL portions of methylene chloride. The combined methylene chloride extracts were evaporated to dryness through a Snyder column utilizing a steam bath. One hundred mL of hexane were added to the residue and the resultant hexane was washed with 50 mL of 1 N KOH solution followed by concentrated sulfuric acid as described in the clean-up section.

Soil and Sediment. Ten to 20 g of a well mixed sample was fortified with 2.5 ng ^{37}Cl-TCDD, refluxed with aqueous KOH/ethanol, and extracted as described in the lean tissue procedure. After refluxing and cooling, the solution was decanted into a separatory funnel through a filter funnel packed with glass wool. The boiling flask and the filter funnel were rinsed with two 10-mL portions of ethyl alcohol followed by 20 mL of hexane. The solution was then extracted with four 25-mL portions of hexane which had been previously used to rinse the boiling flask and filter funnel. The combined hexane extracts were then subjected to the acid/base clean-up procedure.

Clean-up Procedure for Acid/Base Extracts. The combined hexane extracts obtained as described in the sample preparation and extraction section were washed with 25 mL of 1 N KOH solution followed by four 50-mL portions of concentrated sulfuric acid. After a 25-mL water wash, the water and hexane layers were neutralized by the addition of powdered Na_2CO_3. The aqueous layer was discarded, and the hexane was dried by passage through a 11 mm i.d. × 500 mm glass column containing 10 cm of anhydrous powdered Na_2CO_3. The hexane was collected in a Kuderna-Danish evaporative concentrator and concentrated to a volume of 3 mL. This concentrate was transferred to an alumina column that had been pre-wetted with 1 mL of hexane. The column was eluted with 6 mL of carbon tetrachloride (discarded) followed by 4 mL of methylene chloride (collected in a 12-mL distillation receiver). The receiver was capped with a micro-Snyder column. A carborundum boiling chip was added and the methylene chloride was evaporated just to dryness by means of a hot water bath. Two separate 2-mL portions of hexane were added to the distillation receiver and each was evaporated just to dryness. The residue was dissolved in 3 mL of hexane and was chromatographed on a second alumina column as just described. The methylene chloride eluant from the second alumina column was evaporated just to dryness. Two mL of benzene were added to the receiver and the solution was concentrated to a volume of 100 µL. The benzene solution was transferred quantitatively to a 2-mL graduated chromaflex sample tube (Kontes Glass Company K-422560). Using a slow stream of dry nitrogen, the benzene solution was carefully concentrated to a volume of 60 µL. This extract was sealed in glass tubing (3 mm i.d. × 7 cm) and was stored at sub 0 °C until analysis by mass spectrometry.

Sample Preparation Using Neutral Procedure. *Fish Tissue.* Tissue samples were ground to obtain a homogeneous sample. A 15-g sample and 150 g of anhydrous granular sodium sulfate were placed into a Waring blender jar and the mixture was blended for 1 min. The mixture was then blended with 50-g portions of dry ice until the sample was thoroughly powdered. The powder was transferred to a flask and 10 ng of ^{37}Cl-TCDD were added directly onto the powder. The blender jar was rinsed with acetonitrile, and the rinsings plus enough additional acetonitrile to make up exactly 150 mL were added to the flask. After vigorous magnetic stirring for 2 h the mixture was filtered through a glass filter tube (42 × 160 mm) containing approximately 30 g of anhydrous granular sodium sulfate.

Clean-Up Procedure for Neutral Extract. Exactly 100 mL of the acetonitrile extract (representing 10 g of sample) obtained in the previous section were partitioned (*12*) with 50 mL of acetonitrile-saturated hexane. The hexane was then partitioned with two 100-mL portions followed by one 50-mL portion of hexane-saturated acetonitrile. All acetonitrile layers (350 mL total) were combined and re-partitioned with 10 mL of acetonitrile-saturated hexane. Using a Snyder column, the acetonitrile was concentrated to a volume of 10 mL on an explosion-proof hotplate. The residue was taken up in two separate 100-mL portions of hexane and each was concentrated to a volume of 5 to 10 mL. The hexane residue was transferred to a Florisil column, using three 5-mL portions of hexane. The column was washed with

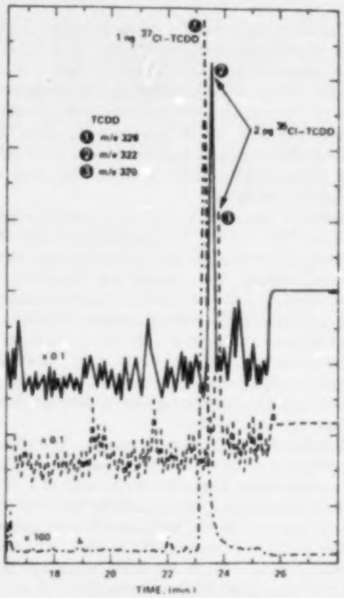

Figure 1. Capillary column GC/HRMS multiple ion selection chromatogram representing 1 ng ^{37}Cl-TCDD and 2 pg TCDD quantification standard

100 mL of 10% methylene chloride in hexane (v/v) and the washings were discarded. The column was eluted with 100 mL of 25% methylene chloride in hexane (v/v). The eluate was collected in a Kuderna-Danish evaporator and was concentrated to a volume of 3 mL utilizing a steam bath. The residue was dissolved in 100 mL of hexane and was concentrated to a volume of 3 mL. The hexane residue was transferred to an alumina column and cleaned up as described in the acid/base procedure with the exception that only one alumina column was used.

DISCUSSION AND RESULTS

Glass capillary columns enhanced the GC-HRMS MIS method of analysis by (1) providing the required resolution of complex mixtures into individual components before they entered the MS; (2) the narrow band width of the TCDD component enhanced MS sensitivity; (3) direct coupling of capillary column to MS ensured maximum transfer efficiency; (4) capillary column bleed rate was low; therefore, background contamination was minimized and the MS sensitivity was enhanced. The requirements imposed on the MS utilized as a GC detector in these analyses were (1) extremely stable electronic circuits; (2) ultra high sensitivity; (3) specific mass detection. The requirements were satisfied by optimizing all components that influenced sensitivity, noise, and mass resolution. The MIS response for a quantification standard, ^{37}Cl-TCDD and TCDD is shown in Figure 1.

Samples collected from highly contaminated sources, i.e., chemical dump sites or fish from contaminated rivers, present serious problems. The high concentrations of chlorinated compounds overload the acid/base clean-up procedure and many compounds are co-extractable with TCDD. These components cause capillary column overload, co-elution of components, etc. The highly specific neutral clean-up procedure was developed and applied to a number of these samples to provide additional confirmation of TCDD residues. It was very effective for this specific isolation of TCDD from other chlorinated components but has not been validated for quantitative TCDD analysis using multiple laboratory participation.

Quantification of TCDD. The MIS simultaneous peak height responses, m/z 328, m/z 322, and m/z 320, of sample and the sample fortified with known amounts of ^{37}Cl-TCDD and TCDD were utilized to determine the percent recovery of ^{37}Cl-TCDD (sample preparation efficiency), TCDD residue level, and limit of detection. The experimental ^{37}Cl-TCDD percent recovery value was used to correct the TCDD residue level and limit of detection for losses in the sample preparation efficiency. A minimum acceptable percent recovery value (50%) for ^{37}Cl-TCDD was established for reporting TCDD analysis. TCDD results were not corrected for recovery values greater than 100%. The occasional ^{37}Cl-TCDD recovery value between 100% and 135%, was attributed to interference from PCBs and unidentified contamination. Typical concentrations of quantification standards were 50 to 300 pg/μL ^{37}Cl-TCDD and 1 to 5 pg/μL TCDD.

Table I. Criteria Utilized for Confirmation of 2,3,7,8-TCDD Residues

1. Correct capillary column GC-HRMS retention time of 2,3,7,8-TCDD.
2. Correct chlorine isotope ratio of the molecular ion (m/z 320 and m/z 322).
3. Correct capillary column GC-HRMS multiple ion monitoring response for TCDD masses and ^{37}Cl-TCDD mass (simultaneous response for elemental composition of m/z 320, m/z 322, and m/z 328).
4. Correct response for co-injection of sample fortified with ^{37}Cl-TCDD and TCDD standard.
5. Response of m/z 320 and m/z 322 must be greater than 2.5 times millimeters of noise level.

Supplemental criteria which may be applied to samples from highly contaminated sources

(A) COCl loss indicative of TCDD structure
(B) Capillary column GC-HRMS peak-matching analysis of m/z 320 and m/z 322 in real time to confirm the TCDD elemental compositions.

Limit of Detection. The minimum limit of detection was defined as the amount of TCDD that would provide clearly defined peak shapes (m/z 320 and m/z 322) in the proper isotopic ratio and with a signal-to-noise ratio greater than 2.5:1. The sample weight, size, percent recovery, sample matrix effects, and electronic noise present in the time frame of measurement does affect the detection limit.

Criteria for Confirmation of TCDD Residues. The capillary column GC-HRMS MIS analysis for 2,3,7,8-TCDD residues must satisfy the criteria, 1–5, shown in Table I to be considered a confirmed positive sample. The supplemental criteria, A and B, were occasionally applied to samples collected from highly contaminated sources.

Purity of ^{37}Cl-TCDD Fortification Standard. A TCDD isomer satisfying the analytical criteria for 2,3,7,8-TCDD (correct retention time and elemental composition) was detected at a concentration level of 1 pg/ng ^{37}Cl-TCDD. These results indicated erroneous sub-ppt TCDD results would be generated for 10-g samples fortified with 10 ng ^{37}Cl-TCDD and this was confirmed experimentally utilizing human milk. The ^{37}Cl-TCDD fortification level was reduced to 2.5 ng to avoid false positive results and provide more accurate quantification of sub-ppt TCDD analyses.

Human Milk Studies. The samples were subjected to the described acid/base extraction and clean-up procedure prior to GC-HRMS MIS analyses. The 60-μL human milk extracts were quantitatively concentrated to 7–20 μL utilizing dry nitrogen gas for sub-ppt TCDD analysis. The MIS analysis sequence was sample, and the sample fortified with ^{37}Cl-TCDD and TCDD. A typical analysis for a QA sample of human mother's milk is shown in Figure 2. The experimental results indicated the sample contained 1.2 ppt TCDD residue. This 10-g sample had been fortified with 10 pg (1 ppt) of

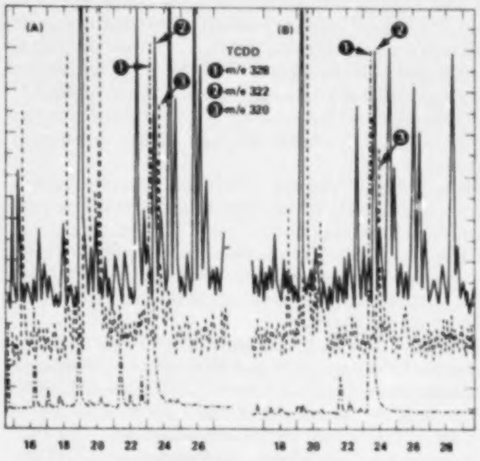

Figure 2. Capillary column GC/HRMS multiple ion selection chromatogram obtained from an extract of QA human milk: (A) 2 μL of sample; (B) 1 μL of sample fortified with ^{37}Cl-TCDD and TCDD quantification standard (QA fortification level, 1 ppt TCDD; experimental result, 1.2 ppt TCDD)

Table II. Typical Analytical Results for 2,3,7,8-TCDD Residues in Quality Assurance Samples[a] of Human Milk

experimental results			TCDD fortification level	
^{37}Cl-TCDD % recovery	TCDD detection limit,[b] ppt	TCDD detected,[b] ppt	pg	ppt
50	0.3	1.9	10	1.0
72	0.2	0.6	3	0.3
68	0.1	0.2	1	0.1
64	0.3	ND	0	0
68	0.4	0.9	9	0.9
84	0.2	1.4	20	2.0
64	0.2	0.4	5	0.5
51	0.2	ND	2	0.2
73	0.4	0.6	7.5	0.75
52	0.3	1.4	6.5	0.65
72	0.5	3.0	30	3.0
100	0.5	4.0	50	5.0
50[c]	0.2	ND	0	0

[a] Each 10-gm sample was fortified with 2.5 ng ^{37}Cl-TCDD. [b] Corrected for % recovery losses. [c] Method blank. ND = not detected, ^{37}Cl-TCDD mean % recovery, 68%. TCDD mean % accuracy, ±38%.

TCDD. The total TCDD analyses (analytical clean-up efficiency, TCDD residue level, and limit of detection) were performed on two sample injections: sample, and fortified sample. Duplicate analyses were usually performed on each sample.

The results of a quality assurance study incorporating human milk fortified with 2.5 ng ^{37}Cl-TCDD and 0 to 5 ppt TCDD are shown in Table II. Evaluation of the experimental results and TCDD fortification level indicate: (1) The sample preparation procedure and MIS method of analysis provided reasonably accurate TCDD analyses in the 0.2 to 5 ppt concentration range considering the amount of TCDD present; (2) False positive results were not detected; (3) 2.5 ng ^{37}Cl-TCDD fortification level was adequate for determining the sample preparation efficiency; (4) The ^{37}Cl-TCDD contamination (2.5 pg TCDD) and corrections for sample preparation efficiency exhibit significant effects in 0 to 1 ppt analyses. Based on recent experiments, the accuracy of 1 ppt TCDD analyses can be improved when the ^{37}Cl-TCDD fortification level is reduced to 0.5 to 1 ng.

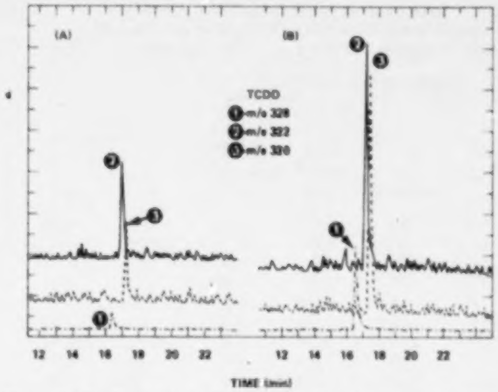

Figure 3. Capillary column GC/HRMS multiple ion selection chromatogram obtained from an extract of ocean perch: (A) sample; (B) sample fortified with ^{37}Cl-TCDD and TCDD quantification standard. The sample had been fortified with 5 ng ^{37}Cl-TCDD and 37 ppt TCDD. The experimental results were: 50% recovery of ^{37}Cl-TCDD; 34 ppt TCDD detected; 4 ppt detection limit

Table III. Typical Analytical Results for Quality Assurance Samples Generated during the Analysis of Fish for 2,3,7,8-TCDD Residues

experimental results				TCDD fortification level	
sample weight, g, and ID	^{37}Cl-TCDD % recovery[a]	TCDD detection limit, ppt[b]	TCDD detected, ppt[b]	pg	ppt
5 (1)[c]	62	2	20	110	22
5 (1)	52	4	34	185	35
5 (1)	82	3	ND	0	0
5 (4)	100	3	ND	0	0
5 (3)	54	1	19	70	14
5 (3)	100	2	ND	0	0
5 (3)	78	2	ND	0	0
5 (1)	92	2	19	55	11
5 (1)	97	5	45	240	48
10 (1)	100+	1	8	130	13
10 (1)	100+	4	43	600	60
10 (2)	100+	7	ND	0	0
10 (2)	100+	3	ND	0	0
10 (1)	100+	4	76	1250	125
10 (4)	67	1	ND	0	0
10 (1)	93	3	56	650	65
10 (1)	84	4	73	620	62

[a] Each sample has been fortified with 5 or 10 ng ^{37}Cl-TCDD. [b] Corrected for % recovery losses, ND = not detected. ^{37}Cl-TCDD mean % recovery, 86%, TCDD mean % accuracy, ±15%. [c] (1) Ocean perch, (2) lake trout, (3) beef liver, (4) method blank.

Fish, Water, and Sediment Analyses. The samples were subjected to the described preparation procedure. A GC-HRMS MIS analysis of a fish extract and the extract fortified with ^{37}Cl-TCDD and TCDD quantification standard is shown in Figure 3. Unusual and high concentrations of chlorinated contaminate masses differing from the exact mass of TCDD were detected in fish collected from polluted waters. The high concentration of co-extractable chlorinated components in fish caused serious problems. To minimize and/or cancel the effects, a small sample size and very high MS sensitivity was utilized. The analytical results generated for QA samples during these studies are shown in Table III. Evaluation of QA results indicate reasonably accurate TCDD results were

Table IV. Typical Analytical Results for Quality Assurance Samples Generated during the Analysis of Water and Sediment for 2,3,7,8-TCDD Results

experimental results					
sample weight, g, and ID	^{37}Cl-TCDD,[a] % recovery	TCDD detection limit[b] ppt	TCDD detected,[b] ppt	TCDD fortification level	
				pg	ppt
1000 (1)[c]	73	0.02	0.0[illegible]	75	0.08
1000 (1)	90	0.05	0.7	1000	1.0
1000 (1)	66	0.01	ND	10	0.01
1000 (1)	95	0.01	0.05	50	0.05
1000 (1)	78	0.02	0.1	100	0.1
1000 (1)	78	0.02	0.03	25	0.03
1000 (1)	100+	0.04	0.4	500	0.5
50 (2)	69	0.13	1.0	50	1.0
50 (2)	100+	0.14	1.0	70	1.4
10 (2)	100+	0.6	2.5	16	1.6
10 (2)	96	0.5	3.3	46	4.6
10 (2)	100+	2.0	23.0	170	17.0
10 (2)	68	4.0	30.0	350	35.0
10 (2)	100	0.7	ND	0	0

[a] Each sample had been fortified with 2.5 ng ^{37}Cl-TCDD. [b] Corrected for % recovery losses. ND = not detected. ^{37}Cl-TCDD mean % recovery, 87%. TCDD mean % accuracy, ±16%. [c] (1) water, (2) sediment.

obtained and no false positive results were detected. The number of QA samples with zero fortification levels of TCDD were very important because of the unusual and high concentrations of chlorinated contamination. The supplemental criteria, Table I, provide additional confirmation of TCDD residues in the presence of high concentrations of chlorinated contamination.

The analytical results for QA samples, Table IV, were generated during water and sediment studies. Reasonably accurate results were obtained for 0.03 ppt to 1 ppt TCDD in water and 0.5 ppt to 35 ppt TCDD in sediment. Water extracts were very clean. Significant amounts of contamination differing from the exact mass of TCDD were detected in specific sediment extracts but did not interfere with TCDD analysis.

TCDD Isomers. Recent reports (*13–16*) have shown that chlorinated dioxins may be formed in combustion processes. The toxicological properties of the known isomers of TCDD are significantly different; however, the mass spectra are almost identical except in the low mass range (*9*), and the minor difference is not significant in ppt analysis of environmental and biological extracts. Therefore, it is extremely important that TCDD isomers be resolved utilizing highly efficient glass capillary columns before introduction into the MS in order to provide more conclusive identification. The 2,3,7,8-TCDD and the available TCDD isomers may be separated, detected, and/or quantified utilizing the described technique. Unfortunately only a limited number of the 22 TCDD isomers are commercially available. The TCDD isomers utilized in this laboratory for co-injection purposes are 1,2,3,4-, 1,3,6,8-, 2,3,6,8-, and 2,3,7,8-TCDD. The described SE-30 WCOT glass capillary column resolution of TCDD isomers and order of elution was similar to the work reported by Buser in which he used OV-101 glass capillary column GC-MS for chromatographic separation of seven out of nine TCDD isomers. This work showed that two out of eight other TCDD isomers coelute with 2,3,7,8-TCDD on OV-101 and suggests that no single capillary column will be able to separate all 22 TCDD isomers. Confirmation of 2,3,7,8-TCDD in the presence of other TCDD isomers also requires analysis on a second capillary column of different polarity to differentiate between isomers.

Preliminary studies utilizing the acid/base clean-up procedure and nanogram quantities of hexa, hepta, and octa substituted dibenzo-*p*-dioxins (analytical standards) suggest tetra chlorodioxin isomers are not formed from the degradation of higher chlorinated dioxins by the acid/base sample preparation conditions. Also nanogram quantities of 2,4,5-trichlorophenol showed no evidence of condensation to the 2,3,7,8-TCDD under the same acid/base sample preparation conditions.

Contamination. Utilizing the criteria shown in Table I for confirmation of TCDD residues, chlorinated compounds do not present significant problems in TCDD analysis except in 0 to 5 ppt analysis or in rare cases of gross contamination. Neutral clean-up procedures, mass resolution of 14000, and polar or nonpolar capillary columns effectively resolve this type of occasional problem.

In general, PCBs were the contamination of major concern. The mass resolutions ca. 12000 and 45000 required to separate PCB masses 321.8677, 327.8775 from TCDD masses 321.8935, 327.8847 could not be utilized in 0 to 5 ppt analysis due to limitations in instrument design and sensitivity. The PCB interference had obvious effects: (1) Recovery of ^{37}Cl-TCDD was greater than 100%; (2) The TCDD m/z 320, m/z 322 chlorine isotope ratio was destroyed. Corrections for PCB interference could be applied if necessary but at a sacrifice in minimum detection limit. The mass resolution, 5000 to 9000 was sufficient for most TCDD analyses.

The occasional and unexpected sample containing high ppt to ppm levels of TCDD may cause serious contamination problems (glassware, etc.) to other TCDD samples prepared in the laboratory. Erroneous and low ppt TCDD residues may then be detected in succeeding samples as a result even though extremely meticulous glassware cleaning procedures are exercised. Laboratory records, good quality assurance practices, and multiple laboratory participation should detect and/or eliminate these problems.

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7.7 QUALITATIVE ANALYSIS BY GC/MS

For each sample, the subcontractor shall execute a maximum of twenty (20) library searches on compounds not identified for quantitation. The eluants of greater apparent concentration should be tentatively identified via a forward search of the EPA/NIH mass spectral library. (Components with responses less than the internal standard are not required to be searched in this fashion. The tentative identifications (the compound that attained the highest percentage of a perfect match via the mass spectral matching technique employed) should be reported along with its CAS number and its match percent score (match value attained/perfect match score x 100 percent). In addition, the mass spectroscopist shall make a succinct statement of the reasonableness of the identification by reporting with the following coding system:

1. Very unlikely
2. Somewhat unlikely
3. Possible
4. Somewhat likely
5. Very likely

METALS BY ATOMIC ABSORPTION SPECTROSCOPY REPRODUCED FROM "METHODS OF CHEMICAL ANALYSIS FOR WATER AND WASTES," EPA-600/4-79-020

Metals - Atomic Absorption Methods		Page 2 of 83
Antimony	Method 204.1	Page 21 of 83
	Method 204.2	Page 23 of 83
Arsenic	Method 206.2	Page 25 of 83
	Method 206.3	Page 27 of 83
Barium	Method 208.1	Page 29 of 83
	Method 208.2	Page 31 of 83
Beryllium	Method 210.1	Page 33 of 83
	Method 210.2	Page 35 of 83
Cadmium	Method 213.1	Page 37 of 83
	Method 213.2	Page 39 of 83
Chromium	Method 218.1	Page 41 of 83
	Method 218.2	Page 43 of 83
Copper	Method 220.1	Page 45 of 83
	Method 220.2	Page 47 of 83
Lead	Method 239.1	Page 49 of 83
	Method 239.2	Page 51 of 83
Mercury	Method 245.1	Page 53 of 83
	Method 245.2	Page 59 of 83
Nickel	Method 249.1	Page 65 of 83
	Method 249.2	Page 67 of 83
Selenium	Method 270.2	Page 69 of 83
Silver	Method 272.1	Page 72 of 83
	Method 272.2	Page 74 of 83
Thallium	Method 279.1	Page 76 of 83
	Method 279.2	Page 78 of 83
Zinc	Method 289.1	Page 80 of 83
	Method 289.2	Page 82 of 82

METALS

(Atomic Absorption Methods)

1. Scope and Application

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. While drinking waters free of particulate matter may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper pretreatment.

1.2 Detection limits, sensitivity and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The data shown in Table 1, however, provide some indication of the actual concentration ranges measurable by direct aspiration and using furnace techniques. In the majority of instances the concentration range shown in the table by direct aspiration may be extended much lower with scale expansion and conversely extended upwards by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. Lower concentrations may also be determined using the furnace techniques. The concentration ranges given in Table 1 are somewhat dependent on equipment such as the type of spectrophotometer and furnace accessory, the energy source and the degree of electrical expansion of the output signal. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To insure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see 5.2.1) and if detected, treat accordingly using either successive dilution, matrix modification or method of standard additions (see 8.5).

1.3 Where direct aspiration atomic absorption techniques do not provide adequate sensitivity, in addition to the furnace procedure, reference is made to specialized procedures such as the gaseous hydride method for arsenic and selenium, the cold vapor technique for mercury, and the chelation–extraction procedure for selected metals. Reference to approved colorimetric methods is also made.

1.4 Atomic absorption procedures are provided as the methods of choice; however, other instrumental methods have also been shown to be capable of producing precise and accurate analytical data. These instrumental techniques include emission spectroscopy, X-ray fluorescence, spark source mass spectroscopy, and anodic stripping to name but a few. The analyst should be cautioned that these methods are highly specialized techniques requiring a high degree of skill to interpret results and obtain valid data.

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These above mentioned techniques are presently considered as alternate test procedures and approval must be obtained prior to their use.

2. Summary of Method

2.1 In direct aspiration atomic absorption spectroscopy a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp whose cathode is made of the element to be determined is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.2 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy (Spectrochim Acta, *24B* 53, 1969) the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2.1 Preliminary treatment of wastewater and/or industrial effluents is usually necessary because of the complexity and variability of the sample matrix. Suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. When the breakdown of organic material is necessitated, the process should include a wet digestion with nitric acid.

2.2.2 In those instances where complete characterization of a sample is desired, the suspended material must be analyzed separately. This may be accomplished by filtration and acid digestion of the suspended material. Metallic constituents in this acid digest are subsequently determined and the sum of the dissolved plus suspended concentrations will then provide the total concentrations present. The sample should be filtered as soon as possible after collection and the filtrate acidified immediately.

2.2.3 The total sample may also be treated with acid without prior filtration to measure what may be termed "total recoverable" concentrations.

2.3 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms are vaporized and dissociated for absorption in the tube than the flame, the use of small sample volumes or detection of low concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor.

TABLE 1

Atomic Absorption Concentration Ranges[1]

	Direct Aspiration			Furnace Procedure[4, 5]	
Metal	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l	Detection Limit ug/l	Optimum Concentration Range ug/l
Aluminum	0.1	1	5 – 50	3	20 – 200
Antimony	0.2	0.5	1 – 40	3	20 – 300
Arsenic[2]	0.002	–	0.002 – 0.02	1	5 – 100
Barium(p)	0.1	0.4	1 – 20	2	10 – 200
Beryllium	0.005	0.025	0.05 – 2	0.2	1 – 30
Cadmium	0.005	0.025	0.05 – 2	0.1	0.5 – 10
Calcium	0.01	0.08	0.2 – 7	–	– –
Chromium	0.05	0.25	0.5 – 10	1	5 – 100
Cobalt	0.05	0.2	0.5 – 5	1	5 – 100
Copper	0.02	0.1	0.2 – 5	1	5 – 100
Gold	0.1	0.25	0.5 – 20	1	5 – 100
Iridium(p)	3	8	20 – 500	30	100 – 1500
Iron	0.03	0.12	0.3 – 5	1	5 – 100
Lead	0.1	0.5	1 – 20	1	5 – 100
Magnesium	0.001	0.007	0.02 – 0.5	–	– –
Manganese	0.01	0.05	0.1 – 3	0.2	1 – 30
Mercury[3]	0.0002	–	0.0002 – 0.01	–	– –
Molybdenum(p)	0.1	0.4	1 – 40	1	3 – 60
Nickel(p)	0.04	0.15	0.3 – 5	1	5 – 100
Osmium	0.3	1	2 – 100	20	50 – 500
Palladium(p)	0.1	0.25	0.5 – 15	5	20 – 400
Platinum(p)	0.2	2	5 – 75	20	100 – 2000
Potassium	0.01	0.04	0.1 – 2	–	–
Rhenium(p)	5	15	50 – 1000	200	500 – 5000
Rhodium(p)	0.05	0.3	1 – 30	5	20 – 400
Ruthenium	0.2	0.5	1 – 50	20	100 – 2000
Selenium[2]	0.002	–	0.002 – 0.02	2	5 – 100
Silver	0.01	0.06	0.1 – 4	0.2	1 – 25
Sodium	0.002	0.015	0.03 – 1	–	– –
Thallium	0.1	0.5	1 – 20	1	5 – 100
Tin	0.8	4	10 – 300	5	20 – 300
Titanium (p)	0.4	2	5 – 100	10	50 – 500
Vanadium (p)	0.2	0.8	2 – 100	4	10 – 200
Zinc	0.005	0.02	0.05 – 1	0.05	0.2 – 4

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(1) The concentrations shown are not contrived values and should be obtainable with any satisfactory atomic absorption spectrophotometer.

(2) Gaseous hydride method.

(3) Cold vapor technique.

(4) For furnace sensitivity values consult instrument operating manual.

(5) The listed furnace values are those expected when using a 20 ul injection and normal gas flow except in the case of arsenic and selenium where gas interrupt is used. The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

3. Definition of Terms

3.1 Optimum Concentration Range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating condition employed.

3.2 Sensitivity: The concentration in milligrams of metal per liter that produces an absorption of 1%.

3.3 Detection Limit: Detection limits can be expressed as either an instrumental or method parameter. The limiting factor of the former using acid water standards would be the signal to noise ratio and degree of scale expansion used; while the latter would be more affected by the sample matrix and preparation procedure used. The Scientific Apparatus Makers Association (SAMA) has approved the following definition for detection limit: that concentration of an element which would yield an absorbance equal to twice the standard deviation of a series of measurements of a solution, the concentraton of which is distinctly detectable above, but close to blank absorbance measurement. The detection limit values listed in Table I and on the individual analysis sheets are to be considered minimum working limits achievable with the procedures given in this manual. These values may differ from the optimum detection limit reported by the various instrument manufacturers.

3.4 Dissolved Metals: Those constituents (metals) which will pass through a 0.45 u membrane filter.

3.5 Suspended Metals: Those constituents (metals) which are retained by a 0.45 u membrane filter.

3.6 Total Metals: The concentration of metals determined on an unfiltered sample following vigorous digestion (Section 4.1.3), or the sum of the concentrations of metals in both the dissolved and suspended fractions.

3.7 Total Recoverable Metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Section 4.1.4).

4. Sample Handling and Preservation

4.1 For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. The sample bottle whether borosilicate glass, linear polyethylene, polyproplyene or Teflon should be thoroughly washed with detergent and tap water; rinsed with 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and finally deionized distilled water in that order.

NOTE 1: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product—NOCHROMIX—available from Godax Laboratories, 6 Varick St. New York, N.Y. 10013, may be used in place of chromic acid. [Chromic acid should not be used with plastic bottles.]

NOTE 2: If it can be documented through an active analytical quality control program using spiked samples, reagent and sample blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

Before collection of the sample a decision must be made as to the type of data desired, i.e., dissolved, suspended, total or total recoverable. For container preference, maximum holding time and sample preservation at time of collection see Table 1 in the front part of this manual. Drinking water samples containing suspended and setteable material should be prepared using the total recoverable metal procedure (section 4.1.4).

4.1.1 For the determination of dissolved constituents the sample must be filtered through a 0.45 u membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus using plain, non-grid marked, membrane filters are recommended to avoid possible contamination.) Use the first 50–100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of <2. Normally, 3 ml of (1:1) acid per liter should be sufficient to preserve the sample (See Note 3). If hexavalent chromium is to be included in the analytical scheme, a portion of the filtrate should be transferred before acidification to a separate container and analyzed as soon as possible using Method 218.3. Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

NOTE 3: If a precipitate is formed upon acidification, the filtrate should be digested using 4.1.3. Also, it has been suggested (International Biological Program, Symposium on Analytical Methods, Amsterdam, Oct. 1966) that additional acid, as much as 25 ml of conc. HCl/liter, may be required to stabilize certain types of highly buffered samples if they are to be stored for any length of time. Therefore, special precautions should be observed for preservation and storage of unusual samples intended for metal analysis.

4.1.2 For the determination of suspended metals a representative volume of unpreserved sample must be filtered through a 0.45 *u* membrane filter. When considerable suspended material is present, as little as 100 ml of a well mixed sample is filtered. Record the volume filtered and transfer the membrane filter containing the insoluble material to a 250 ml Griffin beaker and add 3 ml conc. redistilled HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 ml of conc. redistilled HNO_3. Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (DO NOT BAKE), add 5 ml distilled HCl (1:1) and warm the beaker gently to dissolve any soluble material. (If the sample is to be analyzed by the furnace procedure, 1 ml of 1:1 distilled HNO_3 per 100 ml dilution should be substituted for the distilled 1:1 HCl.) Wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected concentrations of metals present. This volume will vary depending on the metal to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended" (See Note 4.)

NOTE 4: Certain metals such as antimony arsenic, gold, iridium, mercury, osmium, palladium, platinium, rhenium, rhodium, ruthenium, selenium, silver, thallium, tin and titanium require modification of the digestion procedure and the individual sheets for these metals should be consulted.

4.1.3 For the determination of total metals the sample is acidified with 1:1 redistilled HNO_3 to a pH of less than 2 at the time of collection. The sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50–100 ml of well mixed sample will most probably be sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined.)

Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. redistilled HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3 ml portion of conc. redistilled HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of redistilled 1:1 HCl (5 ml/100 ml of final solution) and warm the beaker to dissolve any precipitate or residue resulting from evaporation. (If the sample is to be analyzed by the furnace procedure, substitute distilled HNO_3 for 1:1 HCl so that the final dilution contains 0.5% (v/v) HNO_3.) Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total" (see Note 4).

4.1.4 To determine total recoverable metals, acidify the entire sample at the time of collection with conc. redistilled HNO_3, 5 ml/1. At the time of analysis a 100 ml aliquot of well mixed sample is transferred to a beaker or flask. Five ml of distilled HCl (1:1) is added and the sample heated on a steam bath or hot plate until the volume has been reduced to 15–20 ml making certain the samples do not boil. (If the sample is being prepared for furnace analysis, the same process should be followed except HCl should be omitted.) After this treatment the sample is filtered to remove silicates and other insoluble material that could clog the atomizer and the volume adjusted to 100 ml. The sample is then ready for analysis. Concentrations so determined shall be reported as "total". (See Notes 4, 5, and 6.)

NOTE 5: The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy certain metal complexes if a colorimetric procedure is to be employed for the final determination. When this is suspect, the more vigorous digestion given in 4.1.3 should be followed.

NOTE 6: For drinking water analyses by direct aspiration, the final volume may be reduced to effect up to a 10X concentration of the sample, provided the total dissolved solids in the original sample do not exceed 500 mg/1, the determination is corrected for any non-specific absorbance and there is no loss by precipitation.

5. Interferences

5.1 Direct Aspiration

5.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium, calcium and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

5.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are primarily employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

5.1.3 The presence of high dissolved solids in the sample may result in an interference from non-atomic absorbance such as light scattering. If background correction is not available, a non-absorbing wavelength should be checked. Preferably, high solids type samples should be extracted (see 5.1.1 and 9.2).

5.1.4 Ionization interferences occur where the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positive charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess of an easily ionized element.

5.1.5 Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-element lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

5.2 Flameless Atomization

5.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference use the following procedure. Withdraw from the sample two equal aliquots. To one of the aliquots add a known amount of analyte and dilute both aliquots to the same predetermined volume. [The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4 while keeping in mind the optimum concentration range of the analysis. Under no circumstances should the dilution be less than 1:1]. The diluted aliquots should then be analyzed and the unspiked results multiplied by the dilution factor should be compared to the original determination. Agreement of the results (within ±10%) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis. Those samples which indicate the presence of interference, should be treated in one or more of the following ways.

a. The samples should be successively diluted and reanalyzed to determine if the interference can be eliminated.

b. The matrix of the sample should be modified in the furnace. Examples are the addition of ammonium nitrate to remove alkali chlorides, ammonium phosphate to retain cadmium, and nickel nitrate for arsenic and selenium analyses [ATOMIC ABSORPTION NEWSLETTER Vol. 14, No. 5, p 127, Sept-Oct 1975]. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

c. Analyze the sample by method of standard additions while noting the precautions and limitations of its use (See 8.5).

5.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either the use of background correction or choosing an alternate wavelength outside the absorption band should eliminate this interference. Non-specific broad band absorption interference can also be compensated for with background correction.

5.2.3 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analysis element.

5.2.4 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way broad band absorption will be minimized.

5.2.5 From anion interference studies in the graphite furnace it is generally accepted that nitrate is the preferred anion. Therefore nitric acid is preferable for any digestion or solubilization step. If another acid in addition to HNO_3 is required a minimum amount should be used. This applies particularly to hydrochloric and to a lesser extent to sulfuric and phosphoric acids.

5.2.6 Carbide formation resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. Molybdenum may be cited as an example. When this takes place, the metal will be released very slowly from the carbide as atomization continues. For molybdenum, one may be required to atomize for 30 seconds or more before the signal returns to baseline levels. This problem is greatly reduced and the sensitivity increased with the use of pyrolytically-coated graphite.

5.2.7 Ionization interferences have to date not been reported with furnace techniques.

5.2.8 For comments on spectral interference see section 5.1.5.

5.2.9 Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in part 6.9 of the Atomic Absorption Methods section of this manual. Pipet tips have been known to be a source of contamination. If suspected, they should be acid soaked with 1:5 HNO_3 and rinsed thoroughly with tap and deionized water. The use of a better grade pipet tip can greatly reduce this problem. It is very important that special attention be given to reagent blanks in both analysis and the correction of analytical results. Lastly, pyrolytic graphite because of the production process and handling can become contaminated. As many as five to possibly ten high temperature burns may be required to clean the tube before use.

6. Apparatus

6.1 Atomic absorption spectrophotometer: Single or dual channel, single-or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip chart recorder.

6.2 Burner: The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

6.3 Hollow cathode lamps: Single element lamps are to be preferred but multi-element lamps may be used. Electrodeless discharge lamps may also be used when available.

6.4 Graphite furnace: Any furnace device capable of reaching the specified temperatures is satisfactory.

6.5 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can be easily recognized.

6.6 Pipets: Microliter with disposable tips. Sizes can range from 5 to 100 microliters as required. **NOTE 7**: Pipet tips which are white in color, do not contain CdS, and have been found suitable for research work are available from Ulster Scientific, Inc. 53 Main St. Highland, NY 12528 (914) 691–7500.

6.7 Pressure-reducing valves: The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

6.8 Separatory flasks: 250 ml, or larger, for extraction with organic solvents.

6.9 Glassware: All glassware, linear polyethylene, polyproplyene or Teflon containers, including sample bottles, should be washed with detergent, rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and deionized distilled water in that order. [See Notes 1 and 2 under (4.1) concerning the use of chromic acid and the cleaning procedure.]

6.10 Borosilicate glass distillation apparatus.

7. Reagents

7.1 Deionized distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

7.2 Nitric acid (conc.): If metal impurities are found to be present, distill reagent grade nitric acid in a borosilicate glass distillation apparatus or use a spectrograde acid.
Caution: Distillation should be performed in hood with protective sash in place.

7.2.1 Nitric Acid (1:1): Prepare a 1:1 dilution with deionized, distilled water by adding the conc. acid to an equal volume of water.

7.3 Hydrochloric acid (1:1): Prepare a 1:1 solution of reagent grade hydrochloric acid and deionized distilled water. If metal impurities are found to be present, distill this mixture from a borosilicate glass distillation apparatus or use a spectrograde acid.

7.4 Stock standard metal solutions: Prepare as directed in (8.1) and under the individual metal procedures. Commercially available stock standard solutions may also be used.

7.5 Calibration standards: Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

7.6 Fuel and oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

7.7 Special reagents for the extraction procedure.

7.7.1 Pyrrolidine dithiocarbamic acid (PDCA) "see footnote": Prepare by adding 18 ml of analytical reagent grade pyrrolidine to 500 ml of chloroform in a liter flask.

The name pyrrolidine dithiocarbamic acid (PDCA), although commonly referenced in the scientific literature is ambiguous. From the chemical reaction of pyrrolidine and carbon disulfide a more proper name would be 1-pyrrolidine carbodithioic acid, PCDA (CAS Registry No. 25769–03–3).

(See **Note 8**) Cool and add 15 ml of carbon disulfide in small portions and with swirling. Dilute to 1 liter with chloroform. The solution can be used for several months if stored in a brown bottle in a refrigerator.

NOTE 8: An acceptable grade of pyrrolidine may be obtained from the Aldrich Chemical Co., 940 West St. Paul Ave., Milwaukee, WI. 53233 (414, 273–3850).

7.7.2 Ammonium hydroxide, 2N: Dilute 3 ml conc. NH_4OH to 100 ml with deionized distilled water.

7.7.3 Bromphenol blue indicator (1g/liter): Dissolve 0.1g bromphenol blue in 100 ml of 50 percent ethanol or isopropanol.

7.7.4 HCl, 2.5% v/v: Dilute 2 ml redistilled HCl to 40 ml with deionized distilled water.

8. Preparation of Standards and Calibration

8.1 Stock standard solutions are prepared from high purity metals, oxides or nonhygroscopic reagent grade salts using deionized distilled water and redistilled nitric or hydrochloric acids. (See individual analysis sheets for specific instruction.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1000 mg of the metal per liter. Commercially available standard solutions may also be used.

8.2 Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least four calibration standards in graduated amounts in the appropriate range. The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. As filtered water samples are preserved with 1:1 redistilled HNO_3 (3 ml per liter), calibration standards for these analyses should be similarly prepared with HNO_3. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal.

8.3 Where the sample matrix is so complex that viscosity, surface tension and components cannot be accurately matched with standards, the method of standard addition must be used. This technique relies on the addition of small, known amounts of the analysis element to portions of the sample—the absorbance difference between those and the original solution giving the slope of the calibration curve. The method of standard addition is described in greater detail in (8.5).

8.4 For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorption of 0 to 80 percent. The correct method is to convert the percent absorption readings to absorbance and plot that value against concentration. The following relationship is used to convert absorption values to absorbance:

absorbance = log (100/%T) = 2–log % T
where % T = 100–% absorption

As the curves are frequently nonlinear, especially at high absorption values, the number of standards should be increased in that portion of the curve.

8.5 Method of Standard Additions: In this method, equal volumes of sample are added to a deionized distilled water blank and to three standards containing different known amounts of the test element. The volume of the blank and the standards must be the same. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Fig. 1.

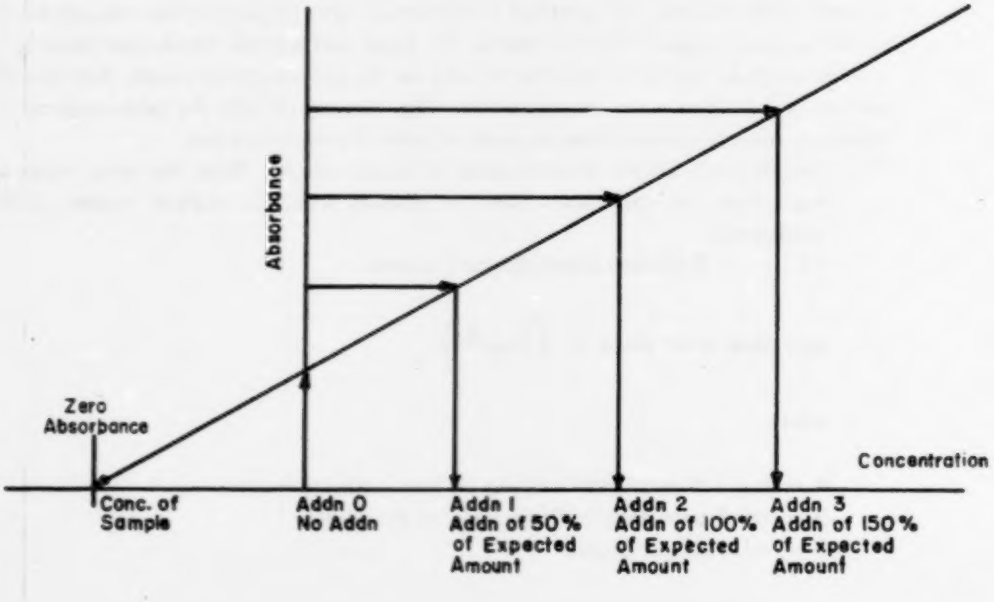
Absorbance
Zero Absorbance
Concentration
Conc. of Sample
Addn 0 No Addn
Addn 1 Addn of 50% of Expected Amount
Addn 2 Addn of 100% of Expected Amount
Addn 3 Addn of 150% of Expected Amount

FIGURE 1. STANDARD ADDITION PLOT

The method of standard additions can be very useful, however, for the results to be valid the following limitations must be taken into consideration:

a) the absorbance plot of sample and standards must be linear over the concentration range of concern. For best results the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20%) caution should be exercised.

b) the effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes and the standard addition should respond in a similar manner as the analyte.

c) the determination must be free of spectral interference and corrected for non-specific background interference.

9. General Procedure for Analysis by Atomic Absorption

9.1 Direct Aspiration: Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for his particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes unless operated in a double beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the manufactuerer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis and construct a calibration curve by plotting the concentrations of the standards against the absorbance. For those instruments which read directly in concentration set the curve corrector to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples are run.

9.1.1 Calculation - Direct determination of liquid samples: Read the metal value in mg/l from the calibration curve or directly from the readout system of the instrument.

9.1.1.1 If dilution of sample was required:

$$\text{mg/l metal in sample} = A\left(\frac{C + B}{C}\right)$$

where:

A = mg/l of metal indiluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

9.1.2 For samples containing particulates:

$$\text{mg/l metal in sample} = A\left(\frac{V}{C}\right)$$

where:

A = mg/l of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
C = ml of sample aliquot processed

9.1.3 For solid samples: report all concentrations as mg/kg dry weight

9.1.3.1 Dry sample:

$$\text{mg metal/kg sample} = \frac{A \times V}{D}$$

where:

A = mg/l of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
D = weight of dry sample in grams

9.1.3.2 Wet sample:

$$\text{mg metal/kg sample} = \frac{A \times V}{W \times P}$$

where:

A = mg/l of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
W = weight of wet sample in grams
P = % solids

9.2 Special Extraction Procedure: When the concentration of the metal is not sufficiently high to determine directly, or when considerable dissolved solids are present in the sample, certain metals may be chelated and extracted with organic solvents. Ammonium pyrrolidine dithiocarbamate (APDC) (see footnote) in methyl isobutyl ketone (MIBK) is widely used for this purpose and is particularly useful for zinc, cadmium, iron, manganese, copper, silver, lead and chromium^{+6}. Tri-valent chromium does not react with APDC unless it has first been converted to the hexavalent form [Atomic Absorption Newsletter *6*, p 128 (1967)]. This procedure is described under method 218.3.

The name ammonium pyrrolidine dithiocarbamate (APDC) is somewhat ambiguous and should more properly be called ammonium, 1-pyrollidine carbodithioate (APCD). CAS Registry No. 5108-96-3.

Aluminum, beryllium, barium and strontium also do not react with APDC. While the **APDC-MIBK** chelating-solvent system can be used satisfactorily, it is possible to experience difficulties. (See Note 9.)

NOTE 9: Certain metal chelates, manganese-APDC in particular, are not stable in MIBK and will redissolve into the aqueous phase on standing. The extraction of other metals is sensitive to both shaking rate and time. As with cadmium, prolonged extraction beyond 1 minute, will reduce the extraction efficiency, whereas 3 minutes of vigorous shaking is required for chromium.

Also, when multiple metals are to be determined either larger sample volumes must be extracted or individual extractions made for each metal being determined. The acid form of APDC-pyrrolidine dithiocarbamic acid prepared directly in chloroform as described by Lakanen, [Atomic Absorption Newsletter *5*, p 17 (1966)], (see 7.7.1) has been found to be most advantageous. In this procedure the more dense chloroform layer allows for easy combination of multiple extractions which are carried out over a broader pH range favorable to multielement extractions. Pyrrolidine dithiocarbamic acid in chloroform is very stable and may be stored in a brown bottle in the refrigerator for months. Because chloroform is used as the solvent, it may not be aspirated into the flame. The following procedure is suggested.

9.2.1 Extraction procedure with pyrrolidine dithiocarbamic acid (PDCA) in chloroform.

9.2.1.1 Transfer 200 ml of sample into a 250 ml separatory funnel, add 2 drops bromphenol blue indicator solution (7.7.3) and mix.

9.2.1.2 Prepare a blank and sufficient standards in the same manner and adjust the volume of each to approximately 200 ml with deionized distilled water. All of the metals to be determined may be combined into single solutions at the appropriate concentration levels.

9.2.1.3 Adjust the pH by addition of 2N NH_4OH solution (7.7.2) until a blue color persists. Add HCl (7.7.4) dropwise until the blue color just disappears; then add 2.0 ml HCl (7.7.4) in excess. The pH at this point should be 2.3. (The pH adjustment may be made with a pH meter instead of using indicator.)

9.2.1.4 Add 5 ml of PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and drain the chloroform layer into a 100 ml beaker. (See NOTE 10.)

NOTE 10: If hexavalent chromium is to be extracted, the aqueous phase must be readjusted back to a pH of 2.3 after the addition of PDCA–chloroform and maintained at that pH throughout the extraction. For multielement extraction, the pH may adjusted upward after the chromium has been extracted.

9.2.1.5 Add a second portion of 5 ml PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and combine the chloroform phase with that obtained in step (9.2.1.4).

9.2.1.6 Determine the pH of the aqueous phase and adjust to 4.5.

9.2.1.7 Repeat step (9.2.1.4) again combining the solvent extracts.

9.2.1.8 Readjust the pH to 5.5, and extract a fourth time. Combine all extracts and evaporate to dryness on a steam bath.

9.2.1.9 Hold the beaker at a 45 degree angle, and slowly add 2 ml of conc. distilled nitric acid, rotating the beaker to effect thorough contact of the acid with the residue.

9.2.1.10 Place the beaker on a low temperature hotplate or steam bath and evaporate just to dryness.

9.2.1.11 Add 2 ml of nitric acid (1:1) to the beaker and heat for 1 minute. Cool, quantitatively transfer the solution to a 10 ml volumetric flask and bring to volume with distilled water. The sample is now ready for analysis.

9.2.2 Prepare a calibration curve by plotting absorbance versus the concentration of the metal standard (*u*g/1) in the 200 ml extracted standard solution. To calculate sample concentration read the metal value in *u*g/1 from the calibration curve or directly from the readout system of the instrument. If dilution of the sample was required use the following equation:

$$\text{mg/l metal in sample} = Z\left(\frac{C + B}{C}\right)$$

where:

Z = *u*g/1 of metal in diluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

9.3 Furnace Procedure: Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instuctions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of his particular instrument and use as a guide the temperature settings and other instrument conditions listed on the individual analysis sheets which are recommended for the Perkin-Elmer HGA-2100. In addition, the following points may be helpful.

9.3.1 With flameless atomization, background correction becomes of high importance especially below 350 nm. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. It can be caused by the presence of gaseous molecular species, salt particules, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

9.3.2 If during atomization all the analyte is not volatilized and removed from the furnace, memory effects will occur. This condition is dependent on several factors such as the volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization and furnace design. If this situation is detected through blank burns, the tube should be cleaned by operating the furnace at full power for the required time period as needed at regular intervals in the analytical scheme.

9.3.3 Some of the smaller size furnace devices, or newer furnaces equipped with feedback temperature control (Instrumentation Laboratories MODEL 555, Perkin-Elmer MODELS HGA 2200 and HGA 76B, and Varian MODEL CRA-90) employing faster rates of atomization, can be operated using lower atomization temperatures for shorter time periods than those listed in this manual.

9.3.4 Although prior digestion of the sample in many cases is not required providing a representative aliquot of sample can be pipeted into the furnace, it will provide for a more uniform matrix and possibly lessen matrix effects.

9.3.5 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

9.3.6 To verify the absence of interference, follow the procedure as given in part 5.2.1.

9.3.7 A check standard should be run approximately after every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Even though tube life depends on sample matrix and atomization temperature, a conservative estimate would be that a tube will last at least 50 firings. A pyrolytic-coating would extend that estimate by a factor of 3.

9.3.8 Calculation–For determination of metal concentration by the furnace: Read the metal value in *ug*/1 from the calibration curve or directly from the readout system of the instrument.

9.3.8.1 If different size furnace injection volumes are used for samples than for standards:

$$ug/l \text{ of metal in sample} = Z\left(\frac{S}{U}\right)$$

where:

Z = *ug*/1 of metal read from calibration curve or readout system
S = ul volume standard injected into furnace for calibration curve
U = ul volume of sample injected for analysis

9.3.8.2 If dilution of sample was required but sample injection volume same as for standard:

$$ug/l \text{ of metal in sample} = Z\left(\frac{C + B}{C}\right)$$

where:

Z = *u*g/l metal in diluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

9.3.9 For sample containing particulates:

$$ug/l \text{ of metal in sample} = Z\left(\frac{V}{C}\right)$$

where:

Z = *u*g/l of metal in processed sample from calibration curve (See 9.3.8.1)
V = final volume of processed sample in ml
C = ml of sample aliquot processed

9.3.10 For solid samples: Report all concentrations as mg/kg dry weight

9.3.10.1 Dry sample:

$$\text{mg metal/kg sample} = \frac{\left(\frac{Z}{1{,}000}\right)V}{D}$$

where:

Z = *u*g/l of metal in processed sample from calibration curve (See 9.3.8.1)
V = final volume of processed sample in ml
D = weight of dry sample in grams

9.3.10.2 Wet sample:

$$\text{mg metal/kg sample} = \frac{\left(\frac{Z}{1{,}000}\right)V}{W \times P}$$

where:

Z = *u*g/l of metal in processed sample from calibration curve (See 9.3.8.1)
V = final volume of processed sample in ml
W = weight of wet sample in grams
P = % solids

10 Quality Control For Drinking Water Analysis

10.1 Minimum requirements

10.1.1 All quality control data should be maintained and available for easy reference or inspection.

10.1.2 An unknown performance sample (when available) must be analyzed once per year for the metals measured. Results must be within the control limit established by EPA. If problems arise, they should be corrected, and a follow-up performance sample should be analyzed.

10.2 Minimum Daily control

10.2.1 After a calibration curve composed of a minimum of a reagent blank and three standards has been prepared, subsequent calibration curves must be verified by use of at least a reagent blank and one standard at or near the MCL. Daily checks must be within ±10 percent of original curve.

10.2.2 If 20 or more samples per day are analyzed, the working standard curve must be verified by running an additional standard at or near the MCL every 20 samples. Checks must be within ±10 percent of original curve.

10.3 Optional Requirements

10.3.1 A current service contract should be in effect on balances and the atomic absorption spectrophotometer.

10.3.2 Class S weights should be available to make periodic checks on balances.

10.3.3 Chemicals should be dated upon receipt of shipment and replaced as needed or before shelf life has been exceeded.

10.3.4 A known reference sample (when available) should be analyzed once per quarter for the metals measured. The measured value should be within the control limits established by EPA.

10.3.5 At least one duplicate sample should be run every 10 samples, or with each set of samples to verify precision of the method. Checks should be within the control limit established by EPA.

10.3.6 Standard deviation should be obtained and documented for all measurements being conducted.

10.3.7 Quality Control charts or a tabulation of mean and standard deviation should be used to document validity of data on a daily basis.

ANTIMONY

Method 204.1 (Atomic absorption, direct aspiration)

STORET NO. Total 01097
Dissolved 01095
Suspended 01096

Optimum Concentration Range: 1–40 mg/l using a wavelength of 217.6 nm
Sensitivity: 0.5 mg/l
Detection Limit: 0.2 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Sb (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Antimony hollow cathode lamp
2. Wavelength: 217.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Fuel lean

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Interferences

1. In the presence of lead (1000 mg/1), a spectral interference may occur at the 217.6 nm resonance line. In this case the 231.1 nm antimony line should be used.
2. Increasing acid concentrations decrease antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards should be matched.

Notes

1. Data to be entered into **STORET** must be reported as *u*g/1.
2. For concentrations of antimony below 0.35 mg/1, the furnace procedure (Method 204.2) is recommended.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 5.0 and 15 mg Sb/1, the standard deviations were ±0.08 and ±0.1, respectively. Recoveries at these levels were 96% and 97%, respectively.

ANTIMONY

Method 204.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01097
Dissolved 01095
Suspended 01096

Optimum Concentration Range: 20–300 ug/1
Detection Limit: 3 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.2% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.3 of the Atomic Absorption Methods section of this manual should be followed including the addition of sufficient 1:1 HCl to dissolve the digested residue for the analysis of suspended or total antimony. The sample solutions used for analysis should contain 2% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–800°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 217.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess of 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

ARSENIC

Method 206.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01002
Dissolved 01000
Suspended 01001

Optimum Concentration Range: 5–100 *ug*/l
Detection Limit: 1 *ug*/l

Preparation of Standard Solution

1. Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 ml of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter. 1 ml = 1 mg As (1000 mg/l).

2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100ml.

3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.

4. Working Arsenic Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2ml of 30% H_2O_2 and 2ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.

2. Cool and bring back to 50 ml with deionized distilled water.

3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace.

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NOTE: If solubilization or digestion is not required, adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30% H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1100°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 193.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
4. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *u*g/l.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent containing 15 *u*g/l and spiked with concentrations of 2, 10 and 25 *u*g/l, recoveries of 85%, 90% and 88% were obtained respectively. The relative standard deviation at these concentrations levels were ±8.8%, ±8.2%, ±3.4% and ±8.7%, respectively.
2. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 20, 50 and 100 *u*g As/l, the standard deviations were ±0.7, ±1.1 and ±1.6 respectively. Recoveries at these levels were 105%, 106% and 101%, respectively.

ARSENIC

Method 206.3 (Atomic Absorption—gaseous hydride)

STORET NO. Total 01002
Dissolved 01000
Suspended 01001

1. Scope and Application
   1.1 The gaseous hydride method determines inorganic arsenic when present in concentrations at or above 2 *ug*/l. The method is applicable to drinking water and most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel and silver.
2. Summary of Method
   2.1 Arsenic in the sample is first reduced to the trivalent form using $SnCl_2$ and converted to arsine, AsH_3, using zinc metal. The gaseous hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the mehtod is 2–20 *ug*/l. The 193.7 nm wavelength line is used.
3. Comments
   3.1 In analyzing drinking water and most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of arsenic to establish adequate recovery.
   3.2 Organic forms of arsenic must be converted to inorganic compounds and organic matter must be oxidized before beginning the analysis. The oxidation procedure given in Method 206.5 (Standard Methods, 14th Edition, Method 404B, p. 285, Procedure 4.a) has been found suitable.
   3.3 For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.
   3.4 For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
   3.5 Data to be entered into STORET must be reported as *ug*/l.
4. Precision and Accuracy
   4.1 Ten replicate solutions of o-arsenilic acid at the 5, 10 and 20 *ug*/l level were analyzed by a single laboratory. Standard deviations were ±0.3, ±0.9 and ±1.1 with recoveries of 94, 93 and 85%, respectively. (Caldwell, J. S., Lishka, R. J., and McFarren, E. F., "Evaluation of a Low Cost Arsenic and Selenium Determination at Microgram per Liter Levels", JAWWA., vol 65, p 731, Nov., 1973.)

Approved for NPDES and SDWA
Issued 1974

5. References

5.1. Except for the perchloric acid step, the procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 14th Edition, p159, Method 301A(VII),(1975)

BARIUM

Method 208.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01007
Dissolved 01005
Suspended 01006

Optimum Concentration Range: 1–20 mg/l using a wavelength of 553.6 nm
Sensitivity: 0.4 mg/l
Detection Limit: 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7787 g barium chloride ($BaCl_2 \cdot 2H_2O$, analytical reagent grade) in deionized distilled water and dilute to 1 liter. 1 ml = 1 mg Ba (1000 mg/l).
2. Potassium chloride solution: Dissolve 95 g potassium chloride, KCl, in deionized distilled water and make up to 1 liter.
3. Prepare dilutions of the stock barium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike add 2.0 ml potassium chloride solution. The calibration standards should be prepared using the same type of acid and the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Barium hollow cathode lamp
2. Wavelength: 553.6 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Approved for NPDES and SDWA
Issued 1974

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Interferences

1. The use of a nitrous oxide-acetylene flame virtually eliminates chemical interference; however, barium is easily ionized in this flame and potassium must be added (1000 mg/1) to standards and samples alike to control this effect.
2. If the nitrous oxide flame is not available and acetylene-air is used, phosphate, silicon and aluminum will severely depress the barium absorbance. This may be overcome by the addition of 2000 mg/1 lanthanum.

Notes

1. Data to be entered into **STORET** must be reported as *u*g/1.
2. For concentrations of barium below 0.2 mg/1, the furnace procedure (Method 208.2) is recommended.
3. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.40 and 2.0 mg Ba/1, the standard deviations were ±0.043 and ±0.13, respectively. Recovereis at these levels were 94% and 113%, respectively.
2. In a round-robin study reported by Standard Methods (13th Edition, p215, method 129A, 1971), three synthetic samples containing barium were analyzed by 13 laboratories. At concentrations of 500, 1000 and 5000 *u*g Ba/1, the reported standard deviations were ±50, ±89 and ±185 *u*g, respectively. The relative error at these concentrations was 8.6%, 2.7% and 1.4%, respectively.

BARIUM

Method 208.2 (Atomic Absorption, furnace technique)

STORET NO. 01007
Dissolved 01005
Suspended 01006

Optimum Concentration Range: 10–200 *ug*/1
Detection Limit: 2 *ug*/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1200°C.
3. Atomizing Time and Temp: 10 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 553.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite.

Approved for NPDES and SDWA
Issued 1978

2. The use of halide acid should be avoided.
3. Because of possible chemical interaction, nitrogen should not be used as a purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 500 and 1000 *ug* Ba/1, the standard deviations were ±2.5 and ±2.2 *ug*, respectively. Recoveries at these levels were 96% and 102%, respectively A dilution of 1:10 was required to bring the spikes within the analytical range of the method.

BERYLLIUM

Methods 210.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01012
Dissolved 01010
Suspended 01011

Optimum Concentration Range: 0.05–2 mg/l using a wavelength of 234.9 nm
Sensitivity: 0.025 mg/l
Detection Limit: 0.005 mg/l

Preparation of Standard Solution

1. Stock solution: Dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in deionized distilled water containing 2 ml conc. nitric acid and dilute to 1 liter. 1 ml = 1 mg Be (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Beryllium hollow cathode lamp
2. Wavelength: 234.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Approved for NPDES
Issued 1974

Interferences

1. Sodium and silicon at concentrations in excess of 1000 mg/1 have been found to severely depress the beryllium absorbance.
2. Bicarbonate ion is reported to interfere; however, its effect is eliminated when samples are acidified to a pH of 1.5.
3. Aluminum at concentrations of 500 *u*g/1 is reported to depress the sensitivity of beryllium [Spectrochim Acta 22, 1325 (1966)].

Notes

1. Data to be entered into **STORET** must be reported as *u*g/1.
2. The "aluminon colorimetric method" may also be used (Standard Methods, 14th Edition, p 177). The minimum detectable concentration by this method is 5 *u*g/1.
3. For concentrations of beryllium below 0.02 mg/1, the furnace procedure (Method 210.2) is recommended.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.01, 0.05 and 0.25 mg Be/1, the standard deviations were ±0.001, ±0.001 and ±0.002, respectively. Recoveries at these levels were 100%, 98% and 97%, respectively.

BERYLLIUM

Method 210.2 (Atomic Absorption, furnace technique)

STORET NO. 01012
Dissolved 01010
Suspended 01011

Optimum Concentration Range: 1–30 ug/l
Detection Limit: 0.2 ug/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1000°C.
3. Atomizing Time and Temp: 10 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 234.9 nm
6. The operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation see "Furnace Procedure" part 9.3 of the Atomic Absorption methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can

Approved for NPDES
Issued 1978

be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Because of possible chemical interaction and reported lower sensitivity, nitrogen should not be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *ug/l*.

Precision and Accuracy

1. Precision and Accuracy data are not available at this time.

CADMIUM

Method 213.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01027
Dissolved 01025
Suspended 01026

Optimum Concentration Range: 0.05–2 mg/l using a wavelength of 228.8 nm
Sensitivity: 0.025 mg/l
Detection Limit: 0.005 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.282 g of cadmium sulfate ($3CdSO_4 \cdot 8H_2O$, analytical reagent grade) and dissolve in deionized distilled water. 1 ml = 1 mg Cd (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Cadmium hollow cathode lamp
2. Wavelength: 228.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Approved for NPDES and SDWA
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Notes

1. For levels of cadmium below 20 ug/1, either the Special Extraction Procedure given in Part 9.2 of the Atomic Absorption methods section as the furnace technique, Method 213.2 is recommended.
2. Data to be entered into **STORET** must be reported as ug/1.
3. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for cadmium were as follows:

Number of Labs	True Values ug/liter	Mean Value ug/liter	Standard Deviation ug/liter	Accuracy as % Bias
74	71	70	21	-2.2
73	78	74	18	-5.7
63	14	16.8	11.0	19.8
68	18	18.3	10.3	1.9
55	1.4	3.3	5.0	135
51	2.8	2.9	2.8	4.7

CADMIUM

Method 213.2 (Atomic Absorption, furnace technique)

STORET NO. 01027
Dissolved 01025
Suspended 01026

Optimum Concentration Range: 0.5–10 *ug/l*
Detection Limit: 0.1 *ug/l*

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Ammonium Phosphate solution (40%): Dissolve 40 grams of ammonium phosphate, $(NH_4)2HPO_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml.
3. Prepare dilutions of the stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike add 2.0 ml of the ammonium phosphate solution. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–500°C.
3. Atomizing Time and Temp: 10 sec–1900°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 228.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Approved for NPDES and SDWA
Issued 1978

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Contamination from the work area is critical in cadmium analysis. Use of pipet tips which are free of cadmium is of particular importance. (See part 5.5.7 of the Atomic Absorption Methods section of this manual.)
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as *u*g/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 2.5, 5.0 and 10.0 *u*g Cd/1, the standard deviations were ±0.10, ±0.16 and ±0.33, respectively. Recoveries at these levels were 96%, 99% and 98%, respectively.

CHROMIUM

Method 218.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01034
Dissolved 01030
Suspended 01031

Optimum Concentration Range: 0.5–10 mg/l using a wavelength of 357.9 nm
Sensitivity: 0.25 mg/l
Detection Limit: 0.05 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.923 g of chromium trioxide (CrO_3, reagent grade) in deionized distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Cr (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Chromium hollow cathode lamp
2. Wavelength: 357.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Approved for NPDES and SDWA
Issued 1971
Editorial revision 1974 and 1978

Notes

1. The following wavelengths may also be used:
   359.3 nm Relative Sensitivity 1.4
   425.4 nm Relative Sensitivity 2
   427.5 nm Relative Sensitivity 3
   428.9 nm Relative Sensitivity 4
2. The fuel rich air–acetylene flame provides greater sensitivity but is subject to chemical and matrix interference from iron, nickel, and other metals. If the analysis is performed in a lean flame the interference can be lessened but the sensitivity will also be reduced.
3. The suppression of both Cr (III) and Cr (VI) absorption by most interfering ions in fuel rich air-acetylene flames is reportedly controlled by the addition of 1% ammonium bifluoride in 0.2% sodium sulfate [Talanta 20, 631 (1973)]. A 1% oxine solution is also reported to be useful.
4. For levels of chromium between 50 and 200 *ug/l* where the air-acetylene flame can not be used or for levels below 50 *ug/l*, either the furnace procedure or the extraction procedure is recommended. See Method 218.2 for the furnace procedure and Method 218.3 for the chelation–extraction procedure.
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into **STORET** must be reported as *ug/l*.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for chromium were as follows:

Number of Labs	True Values *ug/liter*	Mean Value *ug/liter*	Standard Deviation *ug/liter*	Accuracy as % Bias
74	370	353	105	-4.5
76	407	380	128	-6.5
72	74	72	29	-3.1
70	93	84	35	-10.2
47	7.4	10.2	7.8	37.7
47	15.0	16.0	9.0	6.8

CHROMIUM

Method 218.2 (Atomic Absorption, furnace technique)

STORET NO. 01034
Dissolved 01030
Suspended 01031

Optimum Concentration Range: 5–100 *ug*/l
Detection Limit: 1 *ug*/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Calcium Nitrate Solution: Dissolve 11.8 grams of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml. 1 ml = 20 mg Ca.
3. Prepare dilutions of the stock chromium solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3. To each 100 ml of standard and sample alike, add 1 ml of 30% H_2O_2 and 1 ml of the calcium nitrate solution.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods secton of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% v/v HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1000°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 357.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Approved for NPDES and SDWA
Issued 1978

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injecton, continuous flow purge gas and non-pyrolytic graphite.
2. Hydrogen peroxide is added to the acidified solution to convert all chromium to the trivalent state. Calcium is added to a level above 200 mg/1 where its suppressive effect becomes constant up to 1000 mg/1.
3. Background correction may be required if the sample contains high dissolved solids.
4. Nitrogen should not be used as a purge gas because of possible CN band interference.
5. Pipet tips have been reported to be a possible source of contamination. (See part 5.5.7 of the Atomic Absorption Methods section of this manual.)
6. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
7. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
8. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
9. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 19, 48, and 77 *ug* Cr/1, the standard deviations were ±0.1, ±0.2, and ±0.8, respectively. Recoveries at these levels were 97%, 101%, and 102%, respectively.

COPPER

Method 220.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01042
Dissolved 01040
Suspended 01041

Optimum Concentration Range: 0.2–5 mg/l using a wavelength of 324.7 nm
Sensitivity: 0.1 mg/l
Detection Limit: 0.02 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of electrolyte copper (analytical reagent grade). Dissolve in 5 ml redistilled HNO_3 and make up to 1 liter with deionized distilled water. Final concentration is 1 mg Cu per ml (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Copper hollow cathode lamp
2. Wavelength: 324.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Approved for NPDES
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Notes

1. For levels of copper below 50 *ug*/1, either the Special Extraction Procedure, given in part 9.2 of the Atomic Absorption Methods section or the furnace technique, Method 220.2, is recommended.
2. Numerous absorption lines are available for the determination of copper. By selecting a suitable absorption wavelength, copper samples may be analyzed over a very wide range of concentration. The following lines may be used:
   327.4 nm Relative Sensitivity 2
   216.5 nm Relative Sensitivity 7
   222.5 nm Relative Sensitivity 20
3. Data to be entered into **STORET** must be reported as *ug*/1.
4. The 2,9-dimethyl-1, 10-phenanthroline colorimetric method may also be used (Standard Methods, 14th Edition, p. 196).

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for copper were as follows:

Number of Labs	True Values *ug*/liter	Mean Value *ug*/liter	Standard Deviation *ug*/liter	Accuracy as % Bias
91	302	305	56	0.9
92	332	324	56	-2.4
86	60	64	23	7.0
84	75	76	22	1.3
66	7.5	9.7	6.1	29.7
66	12.0	13.9	9.7	15.5

COPPER

Method 220.2 (Atomic Absorption, furnace technique)

STORET NO. 01042
Dissolved 01040
Suspended 01041

Optimum Concentration Range: 5–100 *ug/l*
Detection Limit: 1 *ug/l*

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–900°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 324.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 *ul* injection, continuous flow purge gas and non-pyrolytic

Approved for NPDES
Issued 1978

graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. Background correction may be required if the sample contains high dissolved solids.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

LEAD

Method 239.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01051
Dissolved 01049
Suspended 01050

Optimum Concentration Range: 1–20 mg/1 using a wavelength of 283.3 nm
Sensitivity: 0.5 mg/1
Detection Limit: 0.1 mg/1

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete acidify with 10 ml redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Pb (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Lead hollow cathode lamp
2. Wavelength: 283.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Approved for NPDES and SDWA
Issued 1971
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Notes

1. The analysis of this metal is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust the burner to maximize the absorbance reading with a lead standard. Then, aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal.
2. For levels of lead below 200 *ug*/1, either the Special Extraction Procedure given in part 9.2 of the Atomic Absorption Methods section or the furnace technique, Method 239.2, is recommended.
3. The following lines may also be used:
   217.0 nm Relative Sensitivity 0.4
   261.4 nm Relative Sensitivity 10
4. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
5. Data to be entered into **STORET** must be reported as *ug*/1.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for lead were as follows:

Number of Labs	True Values ug/liter	Mean Value ug/liter	Standard Deviation ug/liter	Accuracy as % Bias
74	367	377	128	2.9
74	334	340	111	1.8
64	101	101	46	-0.2
64	84	85	40	1.1
61	37	41	25	9.6
60	25	31	22	25.7

LEAD
Method 239.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01051
Dissolved 01049
Suspended 01050

Optimum Concentration Range: 5–100 *ug*/l
Detection Limit: 1 *ug*/l

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Lanthanum Nitrate Solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 ml conc. HNO_3 and dilute to 1000 ml with deionized distilled water. 1 ml = 50 mg La.
3. Working Lead Solution: Prepare dilutions of the stock lead solution to be used as calibration standards at the time of analysis. Each calibration standard should contain 0.5% (v/v) HNO_3. To each 100 ml of diluted standard add 10 ml of the lanthanum nitrate solution.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.
2. To each 100 ml of prepared sample solution add 10 ml of the lanthanum nitrate solution.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–500°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 283.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure in the calculation see "Furnace Procedure", part 9.3 of the Atomic Absorption Methods section of this manual.

Approved for NPDES and SDWA
Issued 1978

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 *u*l injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Greater sensitivity can be achieved using the 217.0 nm line, but the optimum concentration range is reduced. The use of a lead electrodeless discharge lamp at this lower wavelength has been found to be advantageous. Also a lower atomization temperature (2400°C) may be preferred.
4. To suppress sulfate interference (up to 1500 ppm) lanthanum is added as the nitrate to both samples and calibration standards. (Atomic Absorption Newsletter Vol. 15, No. 3, p 71, May-June 1976.)
5. Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.
6. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
7. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
8. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
9. Data to be entered into STORET must be reported as *u*g/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 25, 50, and 100 *u*g Pb/1, the standard deviations were ±1.3, ±1.6, and ±3.7, respectively. Recoveries at these levels were 88%, 92%, and 95% respectively.

MERCURY
Method 245.1 (Manual Cold Vapor Technique)

STORET NO. Total 71900
Dissolved 71890
Suspended 71895

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potasssium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.
   1.3 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 *ug* Hg/1 can be achieved; concentrations below this level should be reported as < 0.2 (see Appendix 11.2).
2. Summary of Method
   2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.
3. Sample Handling and Preservation
   3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. If only dissolved mercury is to be determined, the sample should be filtered through an all glass apparatus before the acid is added. For total mercury the filtration is omitted.
4. Interference
   4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/1 of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

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Issued 1974

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/1 had no effect on recovery of mercury from spiked samples.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the **BOD** bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

4.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present (see Appendix 11.1).

5. Apparatus

5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

Note 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4–1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc.: Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content (See Note 3).

NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1 ml = 1 mg Hg.

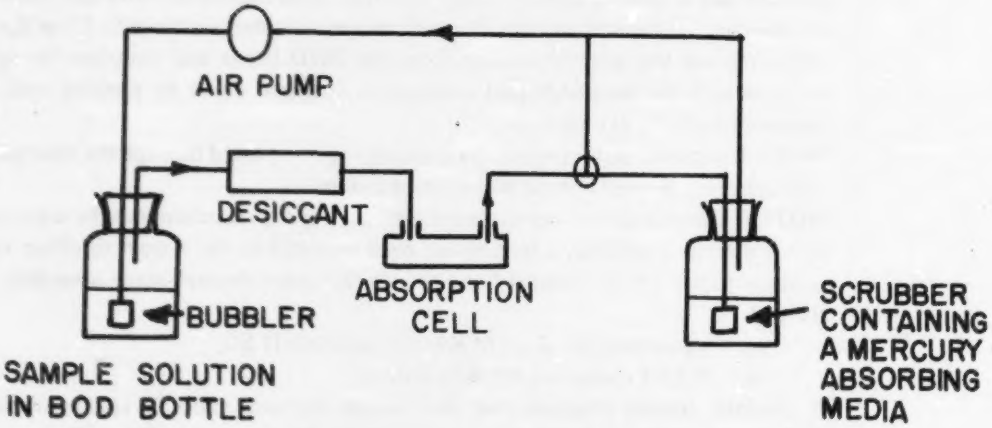
AIR PUMP
DESICCANT
ABSORPTION CELL
BUBBLER
SAMPLE SOLUTION IN BOD BOTTLE
SCRUBBER CONTAINING A MERCURY ABSORBING MEDIA

FIGURE 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10.0 ml aliquots of the working mercury solution containing 0 to 1.0 ug of mercury to a series of 300 ml **BOD** bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) to each bottle. Add 15 ml of $KMnO_4$ (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintined at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 ml of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (See Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the **BOD** bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

a) equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4
b) 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

8. Procedure

8.1 Transfer 100 ml, or an aliquot diluted to 100 ml, containing not more than 1.0 ug of mercury, to a 300 ml **BOD** bottle. Add 5 ml of sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) mixing after each addition. Add 15 ml of potassium permanganate solution (6.5) to each sample bottle. For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. After a delay of at least 30 seconds add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

9. Calculation

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$ug\,\mathrm{Hg/l} = \left(\begin{matrix} ug\,\mathrm{Hg\ in} \\ \mathrm{aliquot} \end{matrix}\right)\left(\frac{1{,}000}{\mathrm{volume\ of\ aliquot\ in\ ml}}\right)$$

9.3 Report mercury concentrations as follows: Below 0.2 *ug*/l, <0.2; between 1 and 10 *ug*/l, one decimal; above 10 *ug*/l, whole numbers.

10. Precision and Accuracy

10.1 In a single laboratory (EMSL), using an Ohio River composite sample with a background mercury concentration of 0.35 *ug*/l, spiked with concentrations of 1.0, 3.0 and 4.0 *ug*/l, the standard deviations were ±0.14, ±0.10 and ±0.08, respectively. Standard deviation at the 0.35 level was ±0.16. Percent recoveries at the three levels were 89, 87, and 87%, respectively.

10.2 In a joint EPA/ASTM interlaboratory study of the cold vapor technique for total mercury in water, increments of organic and inorganic mercury were added to natural waters. Recoveries were determined by difference. A statistical summary of this study follows:

Number of Labs	True Values *ug*/liter	Mean Value *ug*/liter	Standard Deviation *ug*/liter	Accuracy as % Bias
76	0.21	0.349	0.276	66
80	0.27	0.414	0.279	53
82	0.51	0.674	0.541	32
77	0.60	0.709	0.390	18
82	3.4	3.41	1.49	0.34
79	4.1	3.81	1.12	-7.1
79	8.8	8.77	3.69	-0.4
78	9.6	9.10	3.57	-5.2

11. Appendix

11.1 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EMSL has not encountered such samples. This is mentioned only to caution the analyst of the possibility. A simple correction that may be used is as follows: If an interference has been found to be present (4.4), the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

11.2 If additional sensitivity is required, a 200 ml sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 *ug*/l the standard deviations were ±0.027, ±0.006, ±0.01 and ±0.004. Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.

11.3 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water", p 349, Method D3223 (1976).

Bibliography

1. Kopp, J. F., Longbottom, M. C. and Lobring, L. B., "Cold Vapor Method for Determining Mercury", AWWA, vol 64, p. 20, Jan., 1972.
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D3223-73, p 343 (1976).
3. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 156 (1975).

MERCURY

Method 245.2 (Automated Cold Vapor Technique)

STORET NO. Total 71900
Dissolved 71890
Suspended 71895

1. Scope and Application
    - 1.1 This method is applicable to surface waters. It may be applicable to saline waters, wastewaters, effluents, and domestic sewages providing potential interferences are not present (See Interference 4).
    - 1.2 The working range is 0.2 to 20.0 ug Hg/1.
2. Summary of Method
    - 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.
    - 2.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, an automated persulfate oxidation step following the automated addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.
3. Sample Handling and Preservation
    - 3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection.(1) If only dissolved mercury is to be determined, the sample should be filtered before the acid is added. For total mercury the filtration is omitted.
4. Interference (See **NOTE 1**)
    - 4.1 Some sea waters and waste-waters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.
    - 4.2 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run under oxidizing conditions, without stannous sulfate, would determine if this type of interference is present.

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Issued 1974

4.3 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.

4.4 Samples containing solids must be blended and then mixed while being sampled if total mercury vlaues are to be reported.

NOTE 1: All the above interferences can be overcome by use of the Manual Mercury method in this manual.

5. Apparatus

5.1 Technicon Auto Analyzer consisting of:

5.1.1 Sampler II with provision for sample mixing.

5.1.2 Manifold.

5.1.3 Proportioning Pump II or III.

5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116-0163) in series.

5.2 Vapor-liquid separator (Figure 1).

5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.

5.4 Atomic Absorption Spectrophotometer (See Note 2): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 2: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.7 Source of cooling water for jacketed mixing coil and connector A-7.

5.8 Heat lamp: A small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade

6.1.1 Sulfuric acid, 2 N: Dilute 56 ml of conc. sulfuric acid to 1 liter with distilled water.

6.1.2 Sulfuric acid, 10%: Dilute 100 ml conc. sulfuric acid to 1 liter with distilled water.

6.2 Nitric acid, Conc: Reagent grade of low mercury content.

6.2.1 Nitric Acid, 0.5% Wash Solution: Dilute 5 ml of conc. nitric acid to 1 liter with distilled water.

6.3 Stannous Sulfate: Add 50 g stannous sulfate to 500 ml of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.

NOTE 3: Stannous chloride may be used in place of stannous sulfate.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.

NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

6.5 Potassium Permanganate: 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of distilled water.

6.6 Potassium Permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.

6.7 Potassium Persulfate: 0.5% solution, w/v. Dissolve 5 g potassium persulfate in 1 liter of distilled water.

6.8 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml. 1.0 ml = 1.0 mg Hg.

6.9 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.8) to obtain a working standard containing 0.1 *u*g per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 *u*g Hg/1.

6.10 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate (6.6) and 10% sulfuric acid (6.1.2).

7. Procedure

7.1 Set up manifold as shown in Figure 2.

7.2 Feeding all the reagents through the system with acid wash solution (6.2.1) through the sample line, adjust heating bath to 105°C.

7.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.

7.4 Arrange working mercury standards from 0.2 to 20.0 *u*g Hg/1 in sampler and start sampling. Complete loading of sample tray with unknown samples.

7.5 Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as:

a) equal volumes of 0.1 N $KMnO_4$ (6.6) and 10% H_2SO_4 (6.1.2).

b) 0.25% iodine in a 3% KI solution, is recommended.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and North Cassidy St., Columbus, Ohio 43219,
Cat. #580–13 or #580–22.

7.6 After the analysis is complete put all lines except the H_2SO_4 line in distilled water to wash out system. After flushing, wash out the H_2SO_4 line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

8. Precision and Accuracy

8.1 In a single laboratory (SEWL), using distilled water standards at concentrations of 0.5, 1.0, 2.0, 5.0, 10.0 and 20.0 *u*g Hg/l, the standard deviations were ±0.04, ±0.07, ±0.09, ±0.20, ±0.40 and ±0.84 *u*g/l, respectively.

8.2 In a single laboratory (SEWL), using surface water samples spiked with ten organic mercurials at the 10 *u*g/l level, recoveries ranged from 87 to 117%. Recoveries of the same ten organic mercurials in distilled water at the 10 *u*g/l level, ranged from 92% to 125%.

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4. Brandenberger, H. and Bader, H., "The Determination of Mercury by Flameless Atomic Absorption II, A Static Vapor Method", Atomic Absorption Newsletter 7, 53 (1968).
5. Goulden, P. D. and Afghan, B. K., "An Automated Method for Determining Mercury in Water", Technicon, Adv. in Auto. Anal. 2, p 317 (1970).

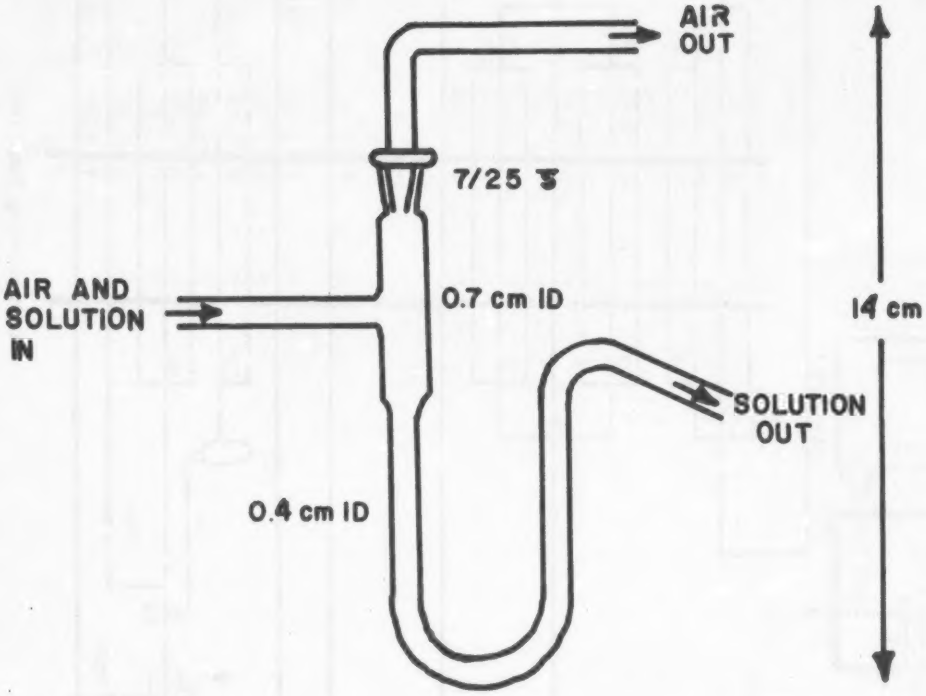
AIR OUT
7/25 ⊊
AIR AND SOLUTION IN
0.7 cm ID
14 cm
SOLUTION OUT
0.4 cm ID

FIGURE 1. VAPOR LIQUID SEPARATOR

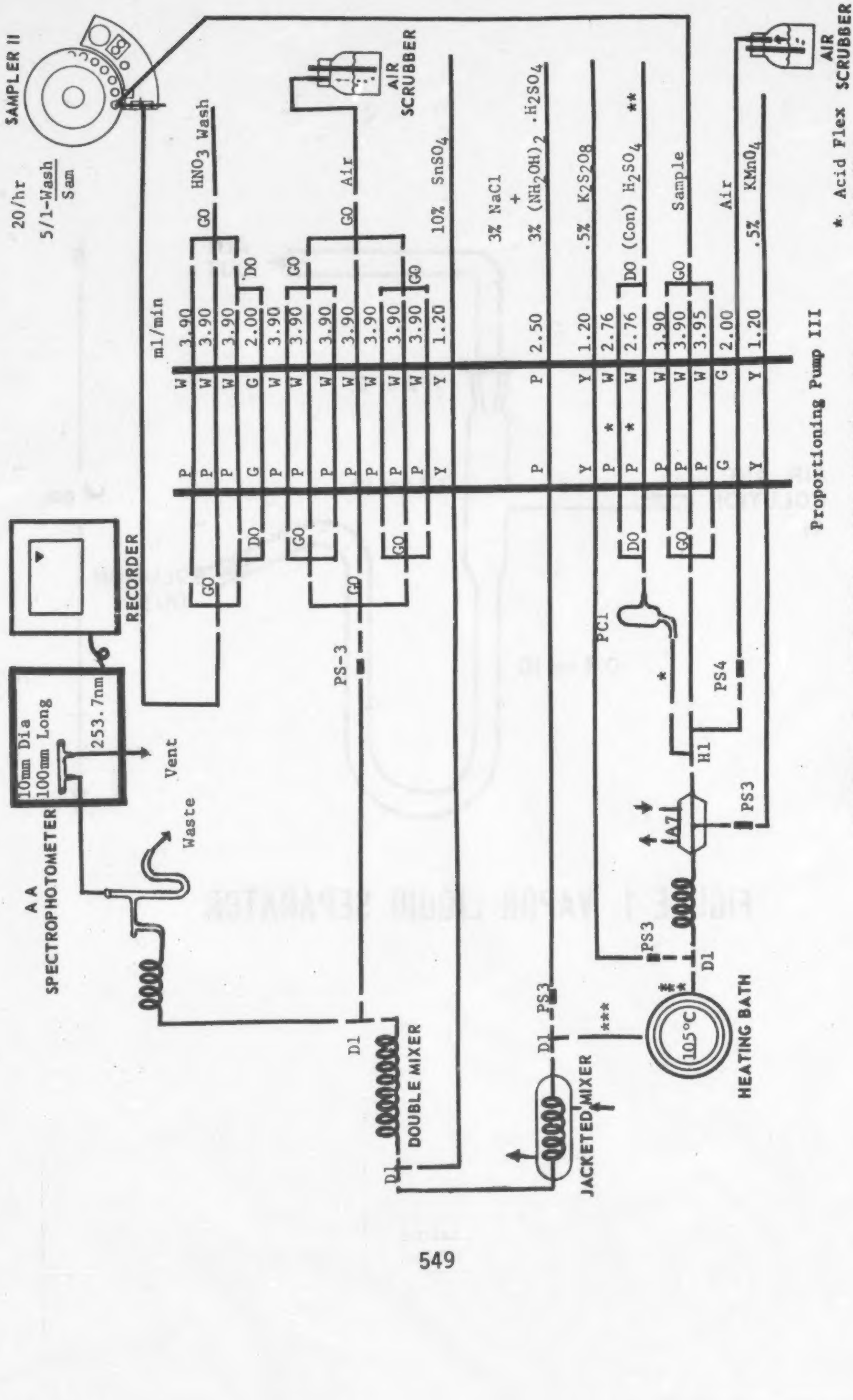
SAMPLER II
20/hr
5/1-Wash/Sam
HNO3 Wash
AIR SCRUBBER
Air
10% SnSO4
3% NaCl + 3% (NH2OH)2 .H2SO4
.5% K2S2O8
(Con) H2SO4 **
Sample
Air
.5% KMnO4
AIR SCRUBBER
ml/min
3.90
3.90
3.90
2.00
3.90
3.90
3.90
3.90
3.90
3.90
1.20
2.50
1.20
2.76
2.76
3.90
3.90
3.95
2.00
1.20
GO
DO
Proportioning Pump III
* Acid Flex
** Teflon
*** Glass
RECORDER
AA SPECTROPHOTOMETER
10mm Dia
100mm Long
253.7nm
Vent
Waste
PS-3
PC1
PS4
H1
A7
PS3
D1
DOUBLE MIXER
JACKETED MIXER
105°C
HEATING BATH

FIGURE 2 MERCURY MANIFOLD AA-I

NICKEL

Method 249.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01067
Dissolved 01065
Suspended 01066

Optimum Concentration Range: 0.3–5 mg/1 using a wavelength of 232.0 nm
Sensitivity: 0.15 mg/1
Detection Limit: 0.04 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.953 g of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ (analytical reagent grade) in deionized distilled water. Add 10 ml of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Ni (1000 mg/1).
2. Prepare dilutions of the stock nickel solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Nickel hollow cathode lamp
2. Wavelength: 232.0 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of Flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Interferences

1. The 352.4 nm wavelength is less susceptible to spectral interference and may be used. The calibration curve is more linear at this wavelength; however, there is some loss of sensitivity.

Notes

1. For levels of nickel below 100 *ug*/1, either the Special Extraction Procedure, given in part 9.2 of the Atomic Absorption Methods section or the furnace technique, Method 249.2, is recommended.
2. Data to be entered into **STORET** must be reported as *ug*/1.
3. The heptoxime method may also be used (Standard Methods, 14th Edition, p 232).

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.20, 1.0 and 5.0 mg Ni/1, the standard deviations were ±0.011, ±0.02 and ±0.04, respectively. Recoveries at these levels were 100%, 97% and 93%, respectively.

NICKEL

Method 249.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01067
Dissolved 01065
Suspended 01066

Optimum Concentration Range: 5–100 *ug/l*
Detection Limit: 1 *ug/l*

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–900°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 232.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic

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graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

SELENIUM

Method 270.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01147
Dissolved 01145
Suspended 01146

Optimum Concentration Range: 5–100 *ug*/l
Detection Limit: 2 *ug*/l

Preparation of Standard Solution

1. Stock Selenium Solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 ml. 1 ml = 1 mg Se (1000 mg/l).
2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 ml.
3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.
4. Working Selenium Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc. HNO_3, 2 ml of 30% H_2O_2 and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.
2. Cool and bring back to 50 ml with deionized distilled water.
3. Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with deionized distilled water. The sample is now ready for injection into the furnace. NOTE: If solubilization or digestion is not required adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30% H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

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Instrument Parameters

1. Drying time and temperature: 30 sec @ 125°C
2. Charring time and temperature: 30 sec @ 1200°C
3. Atomizing time and temperature: 10 sec @ 2700°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 196.0 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Selenium analysis suffers interference from chlorides (> 800 mg/l) and sulfate (> 200 mg/l). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/l, both samples and standards should be prepared to contain 1% nickel.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to entered into STORET must be reported as *ug*/l.

Precision and Accuracy

1. Using a sewage treatment plant effluent containing < 2 *ug*/l and spiked with a concentration of 20 *ug*/l, a recovery of 99% was obtained.
2. Using a series of industrial waste effluents spiked at a 50 *ug*/l level, recoveries ranged from 94 to 112%.
3. Using a 0.1% nickel nitrate solution as a synthetic matrix with selenium concentrations of 5, 10, 20, 40, 50, and 100 *ug*/l, relative standard deviations of 14.2, 11.6, 9.3, 7.2, 6.4 and 4.1%, respectively, were obtained at the 95% confidence level.

4. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 5, 10, and 20 ug Se/1, the standard deviations were ±0.6, ±0.4, and ±0.5, respectively. Recoveries at these levels were 92%, 98%, and 100%, respectively.

Reference:

"Determining Selenium in Water, Wastewater, Sediment and Sludge By Flameless Atomic Absorption Spectroscopy", Martin, T. D., Kopp, J. F. and Ediger, R. D. Atomic Absorption Newsletter 14, 109 (1975).

SILVER

Method 272.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01077
Dissolved 01075
Suspended 01076

Optimum Concentration Range: 0.1–4 mg/1 using a wavelength of 328.1 nm
Sensitivity: 0.06 mg/1
Detection Limit: 0.01 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in deionized distilled water, add 10 ml conc. HNO_3 and make up to 1 liter. 1 ml = 1 mg Ag (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using nitric acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.
3. Iodine Solution, 1 N: Dissolve 20 grams of potassium iodide, KI (analytical reagent grade) in 50 ml of deionized distilled water, add 12.7 grams of iodine, I_2 (analytical reagent grade) and dilute to 100 ml. Store in a brown bottle.
4. Cyanogen Iodide (CNI) Solution: To 50 ml of deionized distilled water add 4.0 ml conc. NH_4OH, 6.5 grams KCN, and 5.0 ml of 1.0 N I_2 solution. Mix and dilute to 100 ml with deionized distilled water. Fresh solution should be prepared every two weeks.(1)

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.3 of the Atomic Absorption Methods section of this manual have been found to be satisfactory; however, the residue must be taken up in dilute nitric acid rather than hydrochloric to prevent precipitation of AgCl.

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Instrumental Parameters (General)

1. Silver hollow cathode lamp
2. Wavelength: 328.1 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. For levels of silver below 30 ug/1, either the Special Extraction Procedure, given in part 9.2 of the Atomic Absorption Methods section or the furnace procedure, Method 272.2, is recommended.
2. Silver nitrate standards are light sensitive. Dilutions of the stock should be discarded after use as concentrations below 10 mg/1 are not stable over long periods of time.
3. If absorption to container walls or the formation of AgCl is suspected, make the sample basic using conc. NH_4OH and add 1 ml of (CNI) solution per 100 ml of sample. Mix the sample and allow to stand for 1 hour before proceeding with the analysis.(1)
4. The 338.2 nm wavelength may also be used. This has a relative sensitivity of 2.
5. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. In a round-robin study reported by Standard Methods, a synthetic sample containing 50 ug Ag/1 was analyzed by 50 laboratories with a reported standard deviation of ±8.8 and a relative error 10.6%.

References

1. "The Use of Cyanogen Iodide (CNI) as a Stabilizing Agent for Silver in Photographic Processing Effluent Sample", Owerbach, Daniel, Photographic Technology Division, Eastman Kodak Company, Rochester, N.Y. 14650.
2. Standard Methods for Examination of Water and Wastewater, 14th Edition, p. 148, Method 301A.

SILVER

Method 272.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01077
Dissolved 01075
Suspended 01076

Optimum Concentration Range: 1–25 *ug*/1
Detection Limit: 0.2 *ug*/1

Preparation of Standard Solution

1. Stock Solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–400°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 328.1 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

THALLIUM

Method 279.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01059
Dissolved 01057
Suspended 01058

Optimum Concentration Range: 5–100 *ug*/1
Detection Limit: 1 *ug*/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 400°C
3. Atomizing Time and Temp: 10 sec @ 2400°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 276.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. For concentrations of thallium below 0.2 mg/1, the furnace procedure, Method 279.2, is recommended.
2. Data to be entered into **STORET** must be reported as *ug*/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.60, 3.0 and 15 mg Tl/1, the standard deviations were ±0.018, ±0.05 and ±0.2, respectively. Recoveries at these levels were 100%, 98% and 98%, respectively.

THALLIUM

Method 279.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01059
Dissolved 01057
Suspended 01058

Optimum Concentration Range: 5–100 ug/1
Detection Limit: 1 ug/1

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C
2. Ashing Time and Temp: 30 sec @ 400°C
3. Atomizing Time and Temp: 10 sec @ 2400°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 276.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

ZINC

Method 289.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01092
Dissolved 01090
Suspended 01091

Optimum Concentration Range: 0.05–1 mg/1 using a wavelength of 213.9 nm
Sensitivity: 0.02 mg/1
Detection Limit: 0.005 mg/1

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of zinc metal (analytical reagent grade) and dissolve cautiously in 10 ml HNO_3. When solution is complete make up to 1 liter with deionized distilled water. 1 ml = 1 mg Zn (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters

1. Zinc hollow cathode lamp
2. Wavelength: 213.9 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For the analysis procedure and the calculation, see "direct aspiration" part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. High levels of silicon may interfere.
2. The air-acetylene flame absorbs about 25% of the energy at the 213.9 nm line.
3. The sensitivity may be increased by the use of low-temperature flames.
4. Some sample container cap liners can be a source of zinc contamination. To circumvent or avoid this problem, the use of polypropylene caps is recommended.
5. The dithizone colorimetric method may also be used (Standard Methods, 14th Edition, p 265).
6. For concentrations of zinc below 0.01 mg/1, either the Special Extraction Procedure given in part 9.2 of the Atomic Absorption Methods section or the furnace procedure, Method 289.2, is recommended.
7. Data to entered into Storet must be reported as *u*g/1.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for zinc were as follows:

Number of Labs	True Values *u*g/liter	Mean Value *u*g/liter	Standard Deviation *u*g/liter	Accuracy as % Bias
86	281	284	97	1.2
89	310	308	114	-0.7
82	56	62	28	11.3
81	70	75	28	6.6
62	7	22	26	206
61	11	17	18	56.6

ZINC

Method 289.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01092
Dissolved 01090
Suspended 01091

Optimum Concentration Range: 0.2–4 *ug/l*
Detection Limit: 0.05 *ug/l*

Preparation of Standard Solution

1. Stock Solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solution for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–400°C.
3. Atomizing Time and Temp: 10 sec–2500°C.
4. Purge Gas Atmosphere: Argon.
5. Wavelength: 213.9 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. The analysis of zinc by the graphite furnace is extremely sensitive and very subject to contamination from the work area, reagents, and pipet tips. Since all these factors affect the precision and accuracy, zinc should be analyzed by the direct aspiration procedure whenever possible.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.